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Hybrid density functionals with proper exact exchange

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Abstract

Hybrid density functionals have the best overall performance among standard density functional approximations (DFA). According to their original design, hybrid DFAs are supposed to use the exact exchange (EXX). However, when hybrid functionals were originally introduced, there was no simple method to compute EXX, so all of their practical implementations started using the Hartree–Fock exchange (HFX), which can be computed easily and is similar to but distinct from EXX. Recent development of an efficient method for computing EXX made it possible to implement hybrid functionals in line with their original definition. We implemented EXX in the PBE0 functional and compared its performance with that of HFX. We found that using EXX in PBE0 improves the standard enthalpies of formation, and this improvement increases with the size of the basis set and the size of the system. The maximum improvement in standard enthalpies of formation of the G3-3 test set is 0.4 kcal/mol when using 6-311++G(3df,3pd) basis set. For a hybrid density functional, the difference in the ground-state energies computed using EXX and HFX depends quadratically on the percentage of EXX in the functional. We have also developed a method to generate the exact remainder exchange-correlation potential of the generalized Kohn–Sham DFT.

Keywords: Kohn–Sham density functional theory, hybrid density functionals, Hartree–Fock exchange, exact exchange, standard enthalpies of formation

Summary for Lay Audience

Quantum chemistry enables one to predict physical and chemical properties of atoms and molecules by solving mathematical equations. Unfortunately, only approximate solutions of those equations can be obtained in practice and they are not always sufficiently accurate for chemical applications. Approximate Kohn–Sham density functional theory (DFT) is the most widely used technique for electronic structure calculations. The accuracy of a DFT calculation depends on the accuracy of the approximate density functional used. Among all such approximations, hybrid density functionals, which combine elements of density-functional and wave-function techniques, have the best overall performance. In most quantum-chemistry software packages, hybrid density functionals are implemented using an approximation for their key ingredient, the so-called exact exchange (EXX), because EXX was originally thought too difficult to compute properly. Recently, an efficient method was invented for computing EXX, which enables us to implement hybrid density functionals properly. In this thesis, we tested the hypothesis that the use of proper EXX in hybrid density functionals improves their performance. We found that it does, but the improvement is modest, which means that there is no compelling reason to abandon the existing approach. We have also demonstrated how the method for computing EXX can be extended to an entire new class of density-functional approximations that go beyond hybrid DFT.

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List of Abbreviations, Symbols, and Nomenclature

DFT	Density functional theory
DFA	Density functional approximation
LSDA	Local spin-density approximation
GGA	Generalized gradient approximation
PBE	Perdew–Burke–Ernzerhof
EXX	Exact exchange
HFX	Hartree–Fock exchange
OEP	Optimized effective potential
RKS	Ryabinkin–Kohut–Staroverov
UGBS	Universal Gaussian basis set
ME	Mean error
MAE	Mean absolute error
PBE0-HFX	PBE0 functional with Hartree–Fock exchange
PBE0-EXX	PBE0 functional with proper exact exchange

Chapter 1

Introduction

Chemistry deals with the structure and properties of systems consisting of electrons and nuclei: atoms, molecules, solids, nanostructures, and molecular assemblies. Quantum chemistry enables one to predict physical and chemical properties of these systems by solving mathematical equations. According to quantum mechanics, all the information about a many-electron system can be extracted from the system's wave function, which in turn can be obtained by solving the corresponding Schrödinger equation. Unfortunately, solving Schrödinger equations exactly is impossible for systems of practical interest. As the famous physicist Paul Dirac said in 1929 [1], “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known. The difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” However, this does not preclude the possibility of solving the Schrödinger equation approximately. The goal of quantum chemistry is to develop approximation techniques for tackling the many-electron problems.

The ground state of a many-electron system is the state with the lowest energy. One way to obtain the ground-state wave function is by searching for the wave function that minimizes the energy. This approach is known as the variational method. Many wave-function methods, such as the Hartree–Fock theory and configuration interaction, are variational techniques.

Wave-function methods can achieve high accuracy; however, the trade-off is their high computational cost. Density functional theory (DFT) is an alternative to the wave-function methods. Calculations using the electron density are generally faster than those involving wave functions, because a wave function of N electrons depends on $3N$ spatial variables, whereas the electron density depends on only 3 variables. In DFT, the ground-state electronic energy of a system is a functional of the electron density of the system. The ground-state electron density can be obtained variationally. However, since the exact energy functional is unknown, one needs to approximate the energy functional in order to use DFT.

In the Kohn–Sham DFT [2], the energy functional is partitioned so that only one term, called the exchange-correlation energy, remains unknown and needs to be approximated. In practice, the exchange-correlation energy is separated into exchange and correlation energy, and these two energies are approximated individually. The Kohn–Sham DFT was proposed in 1965; however, in computational chemistry, functionals that can accurately describe the exchange and correlation energy for chemical systems were not invented until 1990s.

Analytical models for the exchange-correlation energy functional are called density functional approximations (DFA). Among the DFAs, hybrid density functionals have the best overall performance. However, even the results computed using the existing hybrid density functionals are not always accurate enough for chemical purposes. The mean errors in the atomization energies computed using hybrid density functionals are about 2.9–6.7 kcal/mol [3], while the experimental error in atomization energy is usually about 1 kcal/mol. It is highly desirable to improve the hybrid density functional to achieve the experimental level of accuracy is promising. This thesis describes an attempt to improve the performance of hybrid density functionals.

1.1 The fundamentals of quantum chemistry

The foundation of quantum chemistry is the non-relativistic time-independent Schrödinger equation

$$\hat{H}_{\text{tot}}\Psi_{\text{tot}} = E_{\text{tot}}\Psi_{\text{tot}}, \quad (1.1)$$

where \hat{H} is the Hamiltonian operator for the system of electrons and nuclei, E_{tot} is the energy of the system and Ψ is the wave function describing both the electrons and the nuclei. The nuclei are much heavier than the electrons, so they move much more slowly. Therefore, we may assume that the electrons are moving in the field of fixed nuclei. This is known as the Born–Oppenheimer approximation. Under this simplification, we can separate the total Hamiltonian \hat{H}_{tot} into the electronic Hamiltonian \hat{H} , which describes the motion of the electrons for a given nuclear configuration, and the nuclear Hamiltonian. The solution of the Schrödinger equation involving the electronic Hamiltonian,

$$\hat{H}\Psi = E\Psi \quad (1.2)$$

is the electronic wave function Ψ . If we have solved the electronic problem, then we can solve the nuclei problem and obtain the approximate wave function for the nuclei. In this thesis, we focus on the electronic problem.

The electronic Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{\text{en}} + \hat{V}_{\text{ee}} \quad (1.3)$$

$$= -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1.4)$$

where Z_A and \mathbf{R}_A are the atomic number and the position of nucleus A respectively and the vectors \mathbf{r}_i describe the position of the electrons. In Eq. (1.4), the first term describes the kinetic

energy of the electrons, the second term describes the electron-nucleus interaction energy, and the third term describes the electron-electron interaction energy.

The Ψ in Eq. (1.2) is an N -electron wave function. For $N > 1$, solving Eq. (1.2) to obtain Ψ is still too difficult. For $N = 1$, \hat{H} becomes much simpler. Therefore, the electronic problem can be simplified if we can express the N -electron wave function in terms of one-electron wave functions.

1.2 Spin orbitals and spatial orbitals

A one-electron wave function is usually called an orbital. The term “atomic orbital” is applied strictly to atoms, whereas the term “molecular orbital” is often used for both molecules and atoms, particularly when the distinction is unimportant. A spatial orbital $\phi(\mathbf{r})$ describes the spatial distribution of an electron, and $|\phi(\mathbf{r})|^2$ is the probability density of this electron.

To completely describe an electron, we also need to specify its spin. There are two spin states for electrons, spin up and spin down. We use two orthonormal spin functions, $\alpha(\sigma)$ and $\beta(\sigma)$, to describe these states.

A wave function that describes both the spatial distribution and the spin of an electron is a spin orbital. Each spatial orbital can form two spin orbitals, one for spin up and one for spin down, i.e.,

$$\chi(\mathbf{x}) = \begin{cases} \phi(\mathbf{r})\alpha(\sigma) \\ \phi(\mathbf{r})\beta(\sigma) \end{cases} \quad (1.5)$$

Spin orbitals are often used as building blocks for many-electron wave functions.

1.3 Systems of non-interacting electrons

Before discussing systems of interacting electrons, let us consider a simpler system of non-interacting electrons. Such system is essential for understanding many models of quantum chemistry including the Kohn–Sham DFT.

For non-interacting electrons, the Hamiltonian contains only the first and the second terms in Eq. (1.4). The Hamiltonian for non-interacting electrons is separable

$$\hat{H}^0 = \sum_i^N \hat{h}(i), \quad (1.6)$$

where

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \quad (1.7)$$

is a one-electron Hamiltonian that describes the kinetic energy and potential energy of electron i . The operator $\hat{h}(i)$ has a set of eigenfunctions $\{\chi_j(\mathbf{x}_i)\}$,

$$\hat{h}(i)\chi_j(\mathbf{x}_i) = \varepsilon_j\chi_j(\mathbf{x}_i). \quad (1.8)$$

This set of eigenfunctions can be taken as a set of spin orbitals. We normalize the spin orbitals so that

$$\int |\chi_j(\mathbf{x})|^2 d\mathbf{x} = 1 \quad (1.9)$$

Since \hat{H}^0 is a sum of the one-electron Hamiltonian, one can show that the product of spin orbitals of each electron in the system,

$$\Psi^0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_N(\mathbf{x}_N) \quad (1.10)$$

is an eigenfunction of \hat{H}^0 ,

$$\hat{H}\Psi^0 = E\Psi^0 \quad (1.11)$$

with the corresponding eigenvalue being

$$E^0 = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N. \quad (1.12)$$

Eq. (1.10) is not sufficient to represent a system of N electrons properly. According to the Pauli exclusion principle, the wave function of a many-electron system must be anti-symmetric with respect to interchange of any two electrons, i.e.,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N). \quad (1.13)$$

Eq. (1.10) does not satisfy this condition. Fortunately, we can construct an anti-symmetric wave function as an appropriate linear combination of products of spin orbitals. The resulting anti-symmetric wave function is called a Slater determinant

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}, \quad (1.14)$$

where $1/\sqrt{N!}$ is the normalization factor which insures that $\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is normalized

$$\int |\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N = 1. \quad (1.15)$$

One can show that a Slater determinant is also an eigenfunction of $\hat{H}_{\text{elec}}^0 \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$,

$$\hat{H}^0 \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E^0 \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (1.16)$$

with the corresponding eigenvalue being

$$E^0 = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N. \quad (1.17)$$

According to the discussion above, we can conclude that a Slater determinant is an appropriate wave function for N non-interacting electrons.

Since a single Slater determinant can describe a system of N electrons properly, we may use it to approximate the wave function of N interacting electrons. This gives rise to the Hartree–Fock theory, the simplest wave-function method.

1.4 The Hartree–Fock theory

The Hartree–Fock theory approximates the ground-state wave function of an N -electron system by a single a Slater determinant, and provides a recipe for finding this Slater determinant. Since the ground state has the lowest possible electronic energy, for any valid Ψ that represents the electronic system, the corresponding energy satisfies the inequality

$$E = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0, \quad (1.18)$$

where E_0 is the ground-state electronic energy. The equal sign holds only when Ψ is the ground-state wave function, Ψ_0 . This leads to the variational method, where one can obtain the ground-state wave function by systematically varying the wave function until the energy reaches its minimum.

In the Hartree–Fock theory, we need to find the Slater determinant Φ that minimizes the electronic energy

$$E_0^{\text{HF}} = \langle \Phi | \hat{H} | \Phi \rangle. \quad (1.19)$$

This is realized by systematically varying the spin orbitals χ_i , constraining them to be orthonor-

mal, until E_0^{HF} reaches the minimum. For simplicity, we are going to consider a closed-shell system, where each occupied spatial orbital contains two electrons: one spin-up, the other one spin-down. By applying the variational method, one can obtain the equation for the spatial orbitals that minimize E_0^{HF} . This equation is the Hartree–Fock integro-differential equation

$$\hat{f}(\mathbf{r}_1)\varphi_i(\mathbf{r}_1) = \varepsilon_i\varphi_i(\mathbf{r}_1), \quad (1.20)$$

where

$$\hat{f}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + v_{\text{H}}(\mathbf{r}_1) - \hat{K}(\mathbf{r}_1) \quad (1.21)$$

is the Fock operator, $\varphi_i(\mathbf{r}_1)$ is the Hartree–Fock orbital with the corresponding eigenvalue ε_i . The first term in the Fock operator is the one-electron Hamiltonian defined in Eq. (1.7). The second term,

$$v_{\text{H}}(\mathbf{r}_1) = 2 \sum_{j=1}^{N/2} \int \frac{|\varphi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2, \quad (1.22)$$

is the Hartree potential, and \hat{K} is the exchange operator defined as

$$\hat{K}(\mathbf{r}_1)\varphi_i(\mathbf{r}_1) = \sum_{j=1}^{N/2} \left[\int \frac{\varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \varphi_j(\mathbf{r}_1). \quad (1.23)$$

From the equations above we can see that the Fock operator depends on its eigenfunctions. Therefore, Eq. (1.20) has to be solved self-consistently:

1. Make an initial guess for the $N/2$ eigenfunctions $\varphi_i(\mathbf{r})$ of the Fock operator, e.g., by solving the Schrödinger equation for non-interacting electrons.
2. Construct the Fock operator using the current set of eigenfunctions.
3. Solve Eq. (1.20) using the Fock operator constructed in Step 2. Select $N/2$ eigenfunctions with the lowest eigenvalues.
4. If the new eigenfunctions match the eigenfunctions used to construct the Fock operator

within a given threshold, then Eq. (1.20) is self-consistent, and the resulting eigenfunctions are the solutions. If the new eigenfunctions do not match the set of eigenfunctions used to construct the Fock operator, then return to Step 2. The ground-state wave function is the Slater determinant constructed using the spin orbitals that correspond to the $N/2$ spatial orbitals with the lowest eigenvalues.

Once the spatial orbitals φ_i used to construct the ground-state wave function is obtained, we can compute the Hartree–Fock ground-state energy as

$$E_0^{\text{HF}} = T + V + V_{\text{ee}}, \quad (1.24)$$

where

$$T = 2 \sum_{i=1}^{N/2} \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle \quad (1.25)$$

is the kinetic energy,

$$V = 2 \sum_{i=1}^{N/2} \sum_{A=1}^M \int |\varphi_i(\mathbf{r})|^2 \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} d\mathbf{r} \quad (1.26)$$

is the potential energy. The last term, V_{ee} , is the electron–electron interaction energy. It can be separated into two parts. The first part is the Coulomb repulsion energy defined as

$$J = 2 \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (1.27)$$

The remaining part is the Hartree–Fock exchange (HFX) energy, defined as

$$E^{\text{HFX}} = V_{\text{ee}} - J = - \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (1.28)$$

The Hartree–Fock theory yields useful, but not very accurate, predictions of molecular properties. The ground-state electronic energy predicted by the Hartree–Fock theory has an error of about 1% relative to the exact total ground-state electronic energy. 1% relative error seems to be small; however, considering the fact that the absolute value of the exact total

ground-state energy of a molecule is usually more than $100 E_h$, where $1 E_h = 627.5 \text{ kcal/mol} = 2625.5 \text{ kJ/mol}$, the magnitude of this error is too large compared to 1 kcal/mol , the typical experimental error. Therefore we need methods that are more accurate.

Kohn–Sham DFT is an alternative to the Hartree–Fock theory that can achieve a decent accuracy. Since Kohn–Sham DFT also uses single Slater determinant, the mathematical equations in the Kohn–Sham DFT are similar to the Hartree–Fock theory. In Kohn–Sham DFT, the exact exchange (EXX) is equivalent to the HFX. It is more convenient to implement the HFX than the EXX. Therefore, the EXX is approximated by the HFX in practice, with a trade-off in the accuracy. This thesis studies the improvement one can gain by implementing the EXX properly. We will introduce the Kohn–Sham DFT in the next chapter.

Chapter 2

Density functional theory

In 1964, Hohenberg and Kohn [4] proved two far-reaching theorems concerning the electron density. The first theorem states that the electronic energy of the ground state of a many-electron system is a unique functional of the ground-state electron density. The second theorem shows that the ground-state electron density can be obtained using the variational method; the density that minimizes the electronic energy is the ground-state electron density. These theorems gave rise to DFT, which has since become the most widely used method for electronic structure calculations.

The electron density of an N -electron system is defined in terms of the electronic wave function as

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\sigma_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N. \quad (2.1)$$

In DFT, the electronic energy is expressed as a functional of the density. To obtain a formal expression for this energy functional, we may first have a look at the wave-function theory. If the DFT and wave-function theory describe the same system, they should give the same electronic energy, i.e.

$$\langle \Psi | \hat{H} | \Psi \rangle = E[\rho], \quad (2.2)$$

where $\langle \Psi | \hat{H} | \Psi \rangle$ is the electronic energy in wave function theory, and $E[\rho]$ is the energy functional in DFT.

The quantity $\langle \Psi | \hat{H} | \Psi \rangle$ can be separated into three terms,

$$\langle \Psi | \hat{H} | \Psi \rangle = T + V + V_{ee}, \quad (2.3)$$

where

$$T = \langle \Psi | \hat{T} | \Psi \rangle \quad (2.4)$$

is the kinetic energy,

$$V = \langle \Psi | \hat{V}_{en} | \Psi \rangle \quad (2.5)$$

is the potential energy, and

$$V_{ee} = \langle \Psi | \hat{V}_{ee} | \Psi \rangle \quad (2.6)$$

is the electron-electron interaction energy. Let us denote the nuclear potential acting on each electron as

$$v(\mathbf{r}) = \sum_{A=1}^M \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}. \quad (2.7)$$

Then we can rewrite Eq. (2.5) in terms of $\rho(\mathbf{r})$

$$\begin{aligned} V &= \int \cdots \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \left[\sum_{i=1}^N v(\mathbf{r}_i) \right] \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \sum_{i=1}^N \int d\mathbf{r}_i v(\mathbf{r}_i) \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)| d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\sigma_i \cdots \mathbf{x}_N \\ &= \sum_{i=1}^N \frac{1}{N} \int d\mathbf{r}_i v(\mathbf{r}_i) \rho(\mathbf{r}_i) \\ &= \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (2.8)$$

If we separate the ground-state energy functional $E[\rho]$ as

$$E[\rho] = T[\rho] + V[\rho] + V_{ee}[\rho], \quad (2.9)$$

where

$$V[\rho] = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}, \quad (2.10)$$

we can have one term in the ground-state energy functional, $V[\rho]$, expressed exactly. However, the other two terms are still unknown, since we cannot rewrite Eq. (2.4) and (2.6) in terms of $\rho(\mathbf{r})$ explicitly. Therefore, we need to approximate $T[\rho]$ and $V_{\text{ee}}[\rho]$.

2.1 The Kohn–Sham method

For a wave functional that is a single Slater determinant, the kinetic energy is

$$T_s = 2 \sum_{i=1}^{N/2} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle. \quad (2.11)$$

Using this observation, Kohn and Sham [2] suggested to approximate T by T_s and absorb the difference $T - T_s$ into some other term in the energy functional. Specifically, they partitioned the energy functional as

$$\begin{aligned} E[\rho] &= T[\rho] + V[\rho] + V_{\text{ee}}[\rho] \\ &= T_s[\rho] + V[\rho] + J[\rho] + (V_{\text{ee}}[\rho] - J[\rho] + T[\rho] - T_s[\rho]), \end{aligned} \quad (2.12)$$

where

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.13)$$

The term in the parentheses in Eq. (2.12) is called the exchange-correlation energy,

$$E_{\text{XC}}[\rho] = V_{\text{ee}}[\rho] - J[\rho] + T[\rho] - T_s[\rho]. \quad (2.14)$$

Now we can write the energy functional as

$$E[\rho] = T_s[\rho] + V[\rho] + J[\rho] + E_{\text{XC}}[\rho]. \quad (2.15)$$

Eq. (2.15) is formally exact. To use Eq. (2.15) in practice, it is necessary to find the Slater determinant (or orbitals) that computes $T_s[\rho]$ as well as the electron density. Kohn and Sham devised a procedure to obtain them at the same time. They introduced a system of N non-interacting electrons, where the electrons are moving in an external potential $v_{\text{eff}}(\mathbf{r})$. By assuming that the ground-state density of the non-interacting system is the same as the ground-state density of the real interacting system, Kohn and Sham showed that the ground-state density for the real interacting system is

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\phi_i^{\text{KS}}(\mathbf{r})|^2, \quad (2.16)$$

where $\phi_i^{\text{KS}}(\mathbf{r})$ are the Kohn–Sham orbitals obtained by solving the Kohn–Sham eigenvalue problem

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i \phi_i^{\text{KS}}(\mathbf{r}). \quad (2.17)$$

The effective potential $v_{\text{eff}}(\mathbf{r})$ in Kohn–Sham equation is the external potential of the non-interacting system. This effective potential is constructed as

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}), \quad (2.18)$$

where $v(\mathbf{r})$ is the potential of the nuclei,

$$v_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.19)$$

is the Hartree potential, and

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})} \quad (2.20)$$

is the exchange-correlation potential, the functional derivative of the exchange-correlation energy with respect to the density. Similarly to Eq. (1.20), Eq. (2.17) is solved self-consistently.

Note that the exchange-correlation functional in Eq. (2.15) is unknown and has to be approximated. The exchange-correlation energy functional is usually separated into exchange

and correlation parts

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho]. \quad (2.21)$$

The exchange is *defined* by

$$E^{\text{EXX}}[\rho] = - \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \int \int \frac{\phi_i^{\text{KS}*}(\mathbf{r}) \phi_j^{\text{KS}*}(\mathbf{r}') \phi_j^{\text{KS}}(\mathbf{r}) \phi_i^{\text{KS}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (2.22)$$

which is called the exact exchange (EXX). The exact exchange depends on the density implicitly via equation Eq. (2.16). The expression defining the EXX has the same analytic form as Eq. (1.28) defining the HFX. The only difference between EXX and HFX is that the former requires Kohn–Sham orbitals, whereas the latter employs Hartree–Fock orbitals, which are solutions of different eigenvalue problems.

In principle, one can use the EXX for $E_X[\rho]$ and approximate only the correlation functional $E_C[\rho]$. Unfortunately, accurate correlation functionals compatible with the EXX are very difficult to design, so in practice both $E_X[\rho]$ and $E_C[\rho]$ are approximated; their errors largely cancel out each other. For convenience, exchange and correlation are often approximated independently of each other.

2.2 Density-functional approximations

Analytical models for the exchange-correlation energy functional are called density functional approximations (DFA). Depending on which ingredients are involved, DFAs can be classified into various types [5]:

- Local density approximations (LDA): The exchange-correlation energy explicitly depends only on the density ρ

$$E_{XC}[\rho] = \int f(\rho) d\mathbf{r} \quad (2.23)$$

- Generalized gradient approximations (GGA): The exchange-correlation explicitly de-

depends on ρ and the magnitude of the gradient of the density, $|\nabla\rho|$,

$$E_{\text{XC}}[\rho] = \int f(\rho, \nabla\rho) d\mathbf{r} \quad (2.24)$$

- Meta-generalized gradient approximations (meta-GGA): The exchange-correlation depends on ρ , $|\nabla\rho|$, and the kinetic energy density of the non-interacting electrons of the Kohn–Sham system, τ ,

$$E_{\text{XC}}[\rho] = \int f(\rho, \nabla\rho, \tau) d\mathbf{r} \quad (2.25)$$

- Hybrid density functionals: The hybrid density functionals mix the EXX into LDA, GGA or meta-GGA. A typical hybrid density functional have the form

$$E_{\text{XC}}[\rho] = \alpha E^{\text{EXX}}[\rho] + (1 - \alpha) E_{\text{X}}^{\text{DFA}}[\rho] + E_{\text{C}}^{\text{DFA}}[\rho], \quad (2.26)$$

where $0 < \alpha < 1$ is a fitted or non-empirical parameter.

- Double hybrid functionals and other DFAs using both occupied and unoccupied Kohn–Sham orbitals: These DFAs have better overall performance compared to hybrid density functionals but are as expensive as wave-function methods and arguably go beyond the originally intended scope of the Kohn–Sham DFT.

Hybrid density functionals have the best overall performance among DFAs that use only occupied Kohn–Sham orbitals, and are the most commonly used DFAs in chemistry. Before discussing hybrid functionals in more detail, we need to introduce the adiabatic connection approach.

2.3 The adiabatic connection

The adiabatic connection is a bridge between the Kohn–Sham non-interacting reference system and the real interacting physical system. Consider an N -electron system where the electron–electron interaction is scaled by a constant λ ($0 \leq \lambda \leq 1$). The Hamiltonian of this system is

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \lambda \hat{V}_{ee}. \quad (2.27)$$

When $\lambda = 0$, there is no electron–electron interaction; when $\lambda = 1$, the electrons are fully interacting. We are also interested in intermediate cases where λ is between 0 and 1.

In Levy’s constrained-search formulation [6], a universal functional of the density can be defined for each value of λ

$$\begin{aligned} F_\lambda[\rho] &= \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle \\ &= \langle \Psi_{\rho, \min}^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_{\rho, \min}^\lambda \rangle. \end{aligned} \quad (2.28)$$

$F_\lambda[\rho]$ searches over all N -electron wave functions Ψ that yield the N -electron density ρ , and delivers the minimum in the expectation value of $\hat{T} + \lambda \hat{V}_{ee}$. $\Psi_{\rho, \min}^\lambda$ denotes the particular Ψ that minimizes the expectation value of $\hat{T} + \lambda \hat{V}_{ee}$ and yields the density ρ . When $\lambda = 0$, this minimizing wave function is a single Slater determinant (Eq. (1.14)), and we have

$$\begin{aligned} F_0[\rho] &= \langle \Psi_{\rho, \min}^0 | \hat{T} | \Psi_{\rho, \min}^0 \rangle \\ &= 2 \sum_{i=1}^{N/2} \langle \phi_i^{\text{KS}} | -\frac{1}{2} \nabla^2 | \phi_i^{\text{KS}} \rangle = T_s[\rho]. \end{aligned}$$

When $\lambda = 1$, we have

$$F_1[\rho] = T[\rho] + V_{ee}[\rho]. \quad (2.29)$$

Substitution of Eq. (2.29) and (2.29) into Eq. (2.14) gives

$$\begin{aligned} E_{\text{XC}}[\rho] &= F_1[\rho] - F_0[\rho] - J[\rho] \\ &= \int_0^1 \frac{\partial F_\lambda[\rho]}{\partial \lambda} d\lambda - J[\rho] \end{aligned} \quad (2.30)$$

Applying the Hellmann–Feynman theorem [7], one can show that

$$\frac{\partial F_\lambda[\rho]}{\partial \lambda} = \langle \Psi_{\rho,\min}^\lambda | \hat{V}_{\text{ee}} | \Psi_{\rho,\min}^\lambda \rangle. \quad (2.31)$$

Hence

$$E_{\text{XC}}[\rho] = \int_0^1 (\langle \Psi_{\rho,\min}^\lambda | \hat{V}_{\text{ee}} | \Psi_{\rho,\min}^\lambda \rangle - J[\rho]) d\lambda \quad (2.32)$$

Eq. (2.32) is usually written as

$$E_{\text{XC}}[\rho] = \int_0^1 E_{\text{XC}}^\lambda[\rho] d\lambda, \quad (2.33)$$

where

$$E_{\text{XC}}^\lambda[\rho] = \langle \Psi_{\rho,\min}^\lambda | \hat{V}_{\text{ee}} | \Psi_{\rho,\min}^\lambda \rangle - J[\rho]. \quad (2.34)$$

Eq. (2.33) is known as the adiabatic connection formula.

2.4 Hybrid density functionals

The adiabatic connection expresses the exchange-correlation energy as an integral of Eq. (2.33). We do not know how the integrand $E_{\text{XC}}^\lambda[\rho]$ depends on λ . Observing this fact, Becke proposed to approximate the adiabatic connection integral with the upper and lower limits of its integrand using linear interpolation

$$E_{\text{XC}} \simeq \frac{1}{2} E_{\text{XC}}^0 + \frac{1}{2} E_{\text{XC}}^1. \quad (2.35)$$

The lower limit $E_{XC}^0[\rho]$ is precisely the EXX energy functional of Eq. (2.22)

$$E_{XC}^0 = \langle \Psi_{\rho,\min}^0 | \hat{V}_{ee} | \Psi_{\rho,\min}^0 \rangle - J[\rho] = E^{\text{EXX}}[\rho], \quad (2.36)$$

and the upper limit of the integrand Eq. (2.33) is the exchange-correlation energy functional for the real interacting system, which was chosen to be an LDA functional. Eq. (2.35) is the prototype of hybrid density functional. Later, Becke improved this model by reducing the percentage of the EXX and replacing the LDA functional with a GGA functional [8]. He proposed a general form (Eq. (2.26)) for hybrid density functionals. The PBE0 functional [9], a popular GGA hybrid density functional, follows this form

$$E_{XC}^{\text{PBE0}}[\rho] = \frac{1}{4}E^{\text{EXX}}[\rho] + \frac{3}{4}E_X^{\text{PBE}}[\rho] + E_C^{\text{PBE}}[\rho], \quad (2.37)$$

where $E_X^{\text{PBE}}[\rho]$ and $E_C^{\text{PBE}}[\rho]$ are PBE exchange and correlation energy functionals respectively [10, 11]. In this thesis, we use the PBE0 functional as a stand-in representative of all hybrid DFAs.

The hybrid density functionals are originated from the adiabatic connection; therefore, it is supposed to use the EXX, i.e., we need to obtain $\delta E^{\text{EXX}}[\rho]/\delta\rho$ in order to compute the Kohn–Sham orbitals. Unfortunately, $E^{\text{EXX}}[\rho]$ depends on the density implicitly, which means that the functional derivative $\delta E^{\text{EXX}}[\rho]/\delta\rho$ cannot be evaluated analytically. Although there are methods that can numerically compute $\delta E^{\text{EXX}}[\rho]/\delta\rho$, e.g., optimized effective potential (OEP) method [12, 13], the cost of such numerical calculation is rather high. To solve these problems, the HFX came into our sight.

Chapter 3

Hybrid density functionals with proper exact exchange

The equation for exact exchange (Eq. (2.22)) and the HFX (Eq. (1.28)) have the same form. However, they are not identical, since the exact exchange uses Kohn–Sham orbitals, where as the HFX uses the Hartree–Fock orbitals, which are obtained from the Hartree–Fock integro-differential equation (Eq. (1.20)). The Kohn–Sham orbitals and the Hartree–Fock orbitals are obtained by solving different equations and therefore are different.

In principle, the numerical difference between the HFX and the EXX is relatively small. Since using the HFX is a great convenience compare to using the EXX, in all practical implementations including Gaussian 09 [14], hybrid density functionals rely on the HFX as a compromise between adherence to the definition and computational cost. As Becke said in the publication of the first hybrid density functional [15]: “The use of Hartree–Fock orbitals rather than true Kohn–Sham orbitals is admittedly an approximation (a good one, we think) but a great convenience.” Nevertheless, the difference between the EXX and HFX may be significant in practice.

The Kohn–Sham DFT using the EXX-only density functional can be regarded as the Hartree–Fock theory where the HFX is replaced with the EXX and the HFX integral operator with a multiplicative exchange potential. Therefore, the difference in the results computed the Kohn–Sham DFT with the EXX-only density functional and the Hartree–Fock theory reflects the numerical difference between the HFX and the EXX. In 1999, Engel and Dreizler computed

the ground-state energy of atoms using the Kohn–Sham DFT with the EXX-only density functional,

$$E_{\text{XC}}[\rho] = E^{\text{EXX}}[\rho], \quad (3.1)$$

and the Hartree–Fock theory [16]. The results reported by Engel and Dreizler show that the numerical difference between the HFX and the EXX is significant. For Ne atom, the difference in the ground-state energy computed using the EXX-only density functional and Hartree–Fock theory is 1 kcal/mol. For atoms with more electrons, the differences are greater. Since the mean absolute error of hybrid density functionals is already about 3–4 kcal/mol, an additional improvement by 1 kcal/mol (small by itself) could be significant.

Hybrid density functionals typically contain a quarter of the EXX. Hence the numerical difference between using the HFX and the EXX in hybrid density functionals will be much less than 1 kcal/mol for Ne atom. However, for a molecule, this numerical difference should still be significant, since the number of electrons in a molecule is usually several times that for the Ne atom, and the numerical difference between using HFX and EXX in hybrid density functionals increases with the number of electrons in the system. This suggests that implementing the EXX properly in hybrid density functionals may substantially improve the performance of hybrid density functionals.

Our objective is to implement the EXX in the PBE0 functional and compare its performance to the conventional implementation of the PBE0 functional. We are going to denote the EXX-implemented PBE0 functional as PBE0-EXX, and denote the Hartree–Fock-exchange-implemented PBE0 functional as PBE0-HFX.

3.1 Generating exchange-correlation potentials from the wave functions

The main challenge of implementing the EXX is the evaluation of the corresponding exchange potential. The most popular method to numerically compute the EXX potential is the

OEP method [12, 13]. Unfortunately, the OEP method can be ambiguous and numerically unstable when using finite Gaussian basis sets [17]. For this reason, we employed another method to compute the EXX potential. Recently, Ryabinkin *et al.* [18, 19] have developed a method to compute the exact exchange-correlation potentials from electronic wave functions. We will follow their approach to derive a working expression for the EXX potential in a hybrid density functional.

In the following equations, we denote the PBE0-EXX and the PBE0-HFX as 'EXX' and 'HFX' respectively. The Kohn–Sham equation with the proper EXX potential is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}^{\text{hyb}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i^{\text{EXX}} \phi_i(\mathbf{r}). \quad (3.2)$$

We multiply both sides of Eq. (3.2) by $\phi_i^*(\mathbf{r})$, sum over i , and divide through by $\rho^{\text{EXX}}(\mathbf{r})$. The result is the first local energy balance equation

$$\frac{\tau_{\text{L}}^{\text{EXX}}(\mathbf{r})}{\rho^{\text{EXX}}(\mathbf{r})} + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}^{\text{hyb}}(\mathbf{r}) = \bar{\varepsilon}^{\text{KS}}(\mathbf{r}), \quad (3.3)$$

where

$$\tau_{\text{L}}^{\text{EXX}}(\mathbf{r}) = \sum_{i=1}^{N/2} \phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \phi_i(\mathbf{r}) \quad (3.4)$$

is the Kohn–Sham kinetic energy density and

$$\bar{\varepsilon}^{\text{EXX}}(\mathbf{r}) = \frac{2}{\rho^{\text{EXX}}(\mathbf{r})} \sum_{i=1}^{N/2} \varepsilon_i^{\text{EXX}} |\phi_i(\mathbf{r})|^2 \quad (3.5)$$

is the average local Kohn–Sham orbital energy. The second local energy balance equation originated from the Kohn–Sham equation that uses the HFX

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + \frac{1}{4}\hat{K}(\mathbf{r}) + \frac{3}{4}v_{\text{X}}^{\text{PBE}}(\mathbf{r}) + v_{\text{C}}^{\text{PBE}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i^{\text{HFX}} \phi_i(\mathbf{r}). \quad (3.6)$$

We multiply both sides of Eq. (3.6) by $\phi_i^*(\mathbf{r})$, sum over i , and divide through by $\rho^{\text{HFX}}(\mathbf{r})$. This

gives

$$\frac{\tau_L^{\text{HFX}}(\mathbf{r})}{\rho^{\text{HFX}}(\mathbf{r})} + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + \frac{1}{4}v_{\text{X}}^{\text{S}}(\mathbf{r}) + \frac{3}{4}v_{\text{X}}^{\text{PBE}}(\mathbf{r}) + v_{\text{C}}^{\text{PBE}}(\mathbf{r}) = \bar{\epsilon}^{\text{KS}}(\mathbf{r}), \quad (3.7)$$

where

$$v_{\text{X}}^{\text{S}}(\mathbf{r}) = \frac{2}{\rho^{\text{HFX}}(\mathbf{r})} \sum_{i=1}^{N/2} \varphi_i^*(\mathbf{r}) \hat{K}(\mathbf{r}) \varphi(\mathbf{r}) \quad (3.8)$$

is the Slater potential [20], $\tau_L^{\text{HFX}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{HFX}}(\mathbf{r})$ have the same expressions as $\tau_L^{\text{EXX}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{EXX}}(\mathbf{r})$, respectively. Since the two equations describe the same system, we have

$$\rho^{\text{EXX}}(\mathbf{r}) = \rho^{\text{HFX}}(\mathbf{r}). \quad (3.9)$$

Subtracting Eq. (3.7) from Eq. (3.3) and rearranging the terms, we have

$$v_{\text{XC}}^{\text{hyb}}(\mathbf{r}) = \frac{1}{4}v_{\text{X}}^{\text{S}}(\mathbf{r}) + \frac{3}{4}v_{\text{X}}^{\text{PBE}}(\mathbf{r}) + v_{\text{C}}^{\text{PBE}}(\mathbf{r}) + \bar{\epsilon}^{\text{EXX}}(\mathbf{r}) - \bar{\epsilon}^{\text{HFX}}(\mathbf{r}) + \frac{\tau_L^{\text{HFX}}(\mathbf{r})}{\rho^{\text{HFX}}(\mathbf{r})} - \frac{\tau_L^{\text{EXX}}(\mathbf{r})}{\rho^{\text{EXX}}(\mathbf{r})}. \quad (3.10)$$

Eq. (3.10) can be simplified further following the idea of Ospadov *et al.* [18, 19]. First we separate $\tau_L^{\text{EXX}}(\mathbf{r})$ as

$$\tau_L^{\text{EXX}}(\mathbf{r}) = \tau_{\text{W}}^{\text{EXX}}(\mathbf{r}) + \tau_{\text{P}}^{\text{EXX}}(\mathbf{r}) - \frac{1}{4}\nabla^2\rho^{\text{EXX}}(\mathbf{r}), \quad (3.11)$$

where

$$\tau_{\text{W}}^{\text{EXX}}(\mathbf{r}) = \frac{|\nabla^2\rho^{\text{EXX}}(\mathbf{r})|}{8\rho^{\text{EXX}}(\mathbf{r})} \quad (3.12)$$

is the von Weizsäcker noninteracting kinetic-energy density and

$$\tau_{\text{P}}^{\text{EXX}}(\mathbf{r}) = \frac{2}{\rho^{\text{EXX}}(\mathbf{r})} \sum_{i<j}^{N/2} |\phi_i(\mathbf{r})\nabla\phi_j(\mathbf{r}) - \phi_j(\mathbf{r})\nabla\phi_i(\mathbf{r})|^2 \quad (3.13)$$

is the Pauli kinetic-energy density. We also separate $\tau_L^{\text{HFX}}(\mathbf{r})$ as

$$\tau_L^{\text{HFX}}(\mathbf{r}) = \tau_W^{\text{HFX}}(\mathbf{r}) + \tau_P^{\text{HFX}}(\mathbf{r}) - \frac{1}{4}\nabla^2\rho^{\text{EXX}}(\mathbf{r}), \quad (3.14)$$

where $\tau_W^{\text{HFX}}(\mathbf{r})$ and $\tau_P^{\text{HFX}}(\mathbf{r})$ have the same expressions as $\tau_W^{\text{EXX}}(\mathbf{r})$ and $\tau_P^{\text{EXX}}(\mathbf{r})$, respectively. Since $\rho^{\text{EXX}}(\mathbf{r}) = \rho^{\text{HFX}}(\mathbf{r})$, we have $\tau_W^{\text{HFX}}(\mathbf{r}) = \tau_W^{\text{EXX}}(\mathbf{r})$. Substituting Eqs. (3.11) and (3.14) into Eq. (3.10), we have

$$v_{\text{XC}}^{\text{hyb}}(\mathbf{r}) = \frac{1}{4}v_{\text{X}}^{\text{S}}(\mathbf{r}) + \frac{3}{4}v_{\text{X}}^{\text{PBE}}(\mathbf{r}) + v_{\text{C}}^{\text{PBE}}(\mathbf{r}) + \bar{\epsilon}^{\text{EXX}}(\mathbf{r}) - \bar{\epsilon}^{\text{HFX}}(\mathbf{r}) + \frac{\tau_P^{\text{HFX}}(\mathbf{r})}{\rho^{\text{HFX}}(\mathbf{r})} - \frac{\tau_P^{\text{EXX}}(\mathbf{r})}{\rho^{\text{EXX}}(\mathbf{r})}. \quad (3.15)$$

Eq. (3.15) is our working formula for the proper PBE0 exchange-correlation potential. Here, $\phi_i(\mathbf{r})$, ϵ_i^{HFX} and $\rho^{\text{HFX}}(\mathbf{r})$ are obtained by a PBE0-HFX calculation. The quantities $\bar{\epsilon}^{\text{EXX}}(\mathbf{r})$, $\tau_P^{\text{EXX}}(\mathbf{r})$ and $\rho^{\text{EXX}}(\mathbf{r})$ depend on $\phi_i(\mathbf{r})$ and $\epsilon_i^{\text{EXX}}(\mathbf{r})$, which in turn depend on $v_{\text{XC}}^{\text{PBE0}}(\mathbf{r})$. Therefore, Eq. (3.10) has to be solved with Eq. (2.17) simultaneously. The procedure in which the multiplicative exchange-correlation potential corresponding to a hybrid functional is computed via Eq. (3.15) will be referred to as the modified Ryabinkin–Kohut–Staroverov (mRKS) method [18, 19].

We will now show that the mRKS method is as accurate as the OEP method. We list the energies of several atoms computed using the EXX-only density functional with the potential generated by the mRKS and the OEP methods in Table 3.1, where the mRKS values are computed by us using the universal Gaussian basis set (UGBS), and the OEP values are obtained from Ref. 16. For He, Ne, N and P atoms, the energies acquired by these two approaches match each other (within 0.0001 E_{h} , considering the rounding error). For Ar and Kr atoms, the two energies have a difference of 0.0001 E_{h} . This is because that the results in Ref. 16 are computed on numerical grids, which effectively represent the basis-set limit; the large UGBS is only close to the basis set limit. Therefore, the energies obtained using the mRKS method with the UGBS are only close to the basis set limit as well. Since the differences in the energies

are small, we can conclude that our method can reproduce the exchange-correlation potential of the OEP method in the complete basis set limit.

Table 3.1: Atomic energies (in E_h) computed using the EXX-only density functional with the potential generated by mRKS and OEP methods.

Atoms	E^{mRKS}	E^{OEP}
He	-2.8617	-2.8617
Ne	-128.5454	-128.5454
Ar	-526.8123	-526.8122
Kr	-2752.0430	-2752.0429
N	-54.4034	-54.4034
P	-340.7150	-340.7150

3.2 Comparison between PBE0-HFX and PBE0-EXX

3.2.1 Performance comparison for using different basis set

In computational chemistry, basis sets are used in practical implementations of *ab initio* methods. For each calculation, all the unknown orbitals are represented by the linear combinations of the known basis functions. Only the coefficients of basis functions are varied until these orbitals meet our requirement. The molecular orbitals can be expressed *exactly* if the basis set is *complete*. However, a complete basis set contains infinitely many functions, which is impossible to be realized. Hence introducing basis sets in practical calculations is an approximation as we can only use finite basis set in practice.

The accuracy of a calculation depends on the basis set used. The smaller the basis set, the poorer the representation of the orbitals. Using a larger basis set may help achieving higher accuracy, with extra computational time being the price. Therefore, one needs to choose the proper basis set based on the level of desired accuracy.

The mRKS method gives different results for different basis sets [18, 19]. Hence our results for the standard enthalpies of formation computed using the PBE0-EXX will also depend on the basis set we used to compute the ground-state electronic energies, and so does the difference between the PBE0-EXX and the PBE0-HFX standard enthalpies of formation. Here, we used

6-31G*, 6-311+G(2d,p) and 6-311++G(3df,3pd) basis sets as small, medium and large Pople style basis set respectively.

The G3 test set [21] of enthalpies of formation is used to validate computational chemical methods. It contains first-, second- and third-row non-hydrogen molecules, hydrocarbons, substituted hydrocarbons, inorganic hydrides and radicals. The G3 test set has 3 subsets: G3-1, G3-2 and G3-3. The average sizes of the molecules in G3-1, G3-2 and G3-3 subsets are 17.4, 32.5 and 50.5 electrons per molecule respectively. Here, we access the difference between the PBE0-HFX and the PBE0-EXX for each subsets individually.

The standard enthalpy of formation of a molecule is calculated as

$$\begin{aligned} \Delta_f H_{298}^\circ(M) = & E(M) - \sum_A E(A) + \text{ZPE} + H_{298}(M) - H_0(M) \\ & - \sum_A [H_{298}(A) - H_0(A) - \Delta_f H_0^\circ(A)], \end{aligned} \quad (3.16)$$

where the molecule and its constituent atoms are denoted as M and A respectively; ZPE is the zero-point energy of the molecule; H_{298} and H_0 are the enthalpies at 298K and 0K respectively, and their difference is the thermal enthalpy correction; $\Delta_f H_0^\circ$ is the enthalpy of formation at 0K. In this thesis, the energies of the molecules in G3 test set were calculated at the equilibrium B3LYP/6-31G(2df,p) geometries. For molecules, ZPE and thermal enthalpy correction values were calculated at the B3LYP/6-31G(2df,p) Scale=0.9854 level using Opt=Tight and Int(Grid=UltraFine). For atoms, enthalpies of formation at 0 K and thermal enthalpy correction values were taken from Ref. 22.

We computed the standard enthalpies of formation of the 55 G3-1 molecules, 93 G3-2 molecules and 75 G3-3 molecules [21] using the PBE0-HFX and the PBE0-EXX with the basis sets mentioned above and compared them to the experimental results. The detailed results of the standard enthalpies of formation are listed in Appendix A. The summary of these results is shown in Table 3.2 to 3.5. For each basis set, the electronic energy computed using the PBE0-EXX is greater than that computed using the PBE0-HFX for each molecule and atom. For each

molecule, the standard enthalpy of formation calculated using the PBE0-EXX is greater than that computed using the PBE0-HFX. Therefore, the value of mean error (ME) in the PBE0-EXX standard enthalpies of formation is less negative than that in the PBE0-HFX standard enthalpies of formation for each basis set.

For G3-1 test set, the difference between PBE0-EXX and PBE0-HFX is negligible. For G3-2 and G3-3 test sets, the mean absolute error (MAE) in the PBE0-EXX standard enthalpies of formation is less than that in the PBE0-HFX standard enthalpies of formation for each basis set. This means that using the EXX in the PBE0 functional can improve its performance for standard enthalpies of formation. The maximum improvement we obtained is 0.4 kcal/mol for the G3-3 test set when using 6-311++G(3df,3pd) basis set.

Table 3.2: ME and MAE (in kcal/mol) in the standard enthalpies of formation of the G3-1 test set computed by the PBE0-HFX and the PBE0-EXX methods using various Pople style basis sets.

		6-31G*	6-311+G(2d,p)	6-311++G(3df,3pd)
PBE0-HFX	ME	6.09	3.27	1.28
	MAE	6.66	3.88	2.86
PBE0-EXX	ME	6.19	3.37	1.38
	MAE	6.71	3.95	2.88
Difference (EXX-HFX)	ME	0.07	0.10	0.10
	MAE	0.05	0.07	0.02

Table 3.3: ME and MAE (in kcal/mol) in the standard enthalpies of formation of the G3-2 test set computed by the PBE0-HFX and the PBE0-EXX methods using various Pople style basis sets.

		6-31G*	6-311+G(2d,p)	6-311++G(3df,3pd)
PBE0-HFX	ME	-1.88	0.06	-4.61
	MAE	6.03	4.10	6.06
PBE0-EXX	ME	-1.65	0.34	-4.30
	MAE	5.95	4.10	5.82
Difference (EXX-HFX)	ME	0.23	0.28	0.31
	MAE	-0.08	0.00	-0.24

From Table 3.3, 3.4 we can find that the average difference between the PBE0-EXX and

Table 3.4: ME and MAE (in kcal/mol) in the standard enthalpies of formation of the G3-3 test set computed by the PBE0-HFX and the PBE0-EXX methods using various Pople style basis sets.

		6-31G*	6-311+G(2d,p)	6-311++G(3df,3pd)
PBE0-HFX	ME	-5.79	-1.67	-9.28
	MAE	14.07	7.26	10.20
PBE0-EXX	ME	-5.41	-1.20	-8.76
	MAE	13.83	7.15	9.78
Difference (EXX-HFX)	ME	0.38	0.47	0.52
	MAE	-0.24	-0.11	-0.42

Table 3.5: ME and MAE (in kcal/mol) in the standard enthalpies of formation of the G3-3 test set computed by the PBE0-HFX and the PBE0-EXX methods using various Dunning's correlation-consistent basis sets.

		cc-pVDZ	cc-pVTZ	cc-pVQZ
PBE0-HFX	ME	7.35	-2.52	-3.85
	MAE	7.90	4.96	5.41
PBE0-EXX	ME	7.62	-2.23	-3.53
	MAE	8.08	4.79	5.18
Difference (EXX-HFX)	ME	0.27	0.29	0.32
	MAE	0.18	-0.17	-0.23

the PBE0-HFX standard enthalpies of formation generally increases with the size of the basis set. It is because that the magnitude of the difference in the PBE0-EXX and the PBE0-HFX standard enthalpies of formation increases with the size of the basis set used in the calculation. Besides using the Pople style basis sets, we computed the standard enthalpies of formation for G3-2 subset using Dunning's correlation-consistent basis sets cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets, which are listed in an ascending order according to their sizes. The summary of the results is shown in Table 3.5, which matches our finding. The detailed results are listed in Appendix B.

The best improvement we obtained is 0.4 kcal/mol, which is lower than our expectation 1kcal/mol. One of the reasons is that our hypothesis is based on the results computed using the UGBS. To show this, we computed the energies of several atoms using the EXX-only functional and the Hartree-Fock theory with the basis sets mentioned above as well as the

Table 3.6: The difference in the energy (in kcal/mol) for several atoms computed using mRKS method implemented EXX-only density functional and Hartree–Fock theory with several basis sets

Atoms	6-31G*	6-311+G(2d,p)	6-311++G(3df,3pd)	UGBS
Ne	0.33	0.34	0.34	1.05
Ar	0.89	1.47	1.47	3.27
Kr	3.34	4.91	4.98	7.44
N	0.30	0.30	0.30	0.72
P	0.80	1.55	1.55	2.66

UGBS. Their differences are listed in Table 3.6. For 6-311++G(3df,3pd), the differences in the energies are approximately one half of that of UGBS. This suggests that the difference in the PBE0-HFX and PBE0-EXX standard enthalpies of formation computed using UGBS can be close to 1 kcal/mol. This means that our hypothesis is reasonable. However, considering the computational cost, the UGBS is too large to be used in the daily calculations of medium-size molecules.

3.2.2 Performance comparison for molecules of different size

Table 3.7: ME and MAE (in kcal/mol) in the standard enthalpies of formation of the G3-1, G3-2 and G3-3 test set computed by the PBE0-HFX and the PBE0-EXX methods using the 6-311++G(3df,3pd) basis set.

		G3-1	G3-2	G3-3
PBE0-HFX	ME	1.28	-4.61	-9.28
	MAE	2.86	6.06	10.20
PBE0-EXX	ME	1.38	-4.30	-8.76
	MAE	2.88	5.82	9.78
Difference (EXX-HFX)	ME	0.10	0.31	0.52
	MAE	0.02	-0.24	-0.42

As shown before, the numerical difference between the HFX and the EXX depends on the number of electrons in the system. Hence the improvement by implementing the EXX properly in the PBE0 should grow with the system size. We computed the standard enthalpies of formation for G3-1, G3-2 and G3-3 test sets using the PBE0-EXX and the PBE0-HFX to see how the improvement by implementing the EXX properly in the PBE0 functional varies

with the number of electrons in the molecule. Since the 6-311++G(3df,3pd) basis set gives the largest difference between the standard enthalpies of formation computed using the PBE0-EXX and the PBE0-HFX, we used the 6-311++G(3df,3pd) basis set to compute standard enthalpies of formations for the G3-1, G3-2 and G3-3 test sets.

The individual G3 standard enthalpies of formation are listed in Appendix A. The summary appears in Table 3.7. For the G3-1 test set, we find that implementing the EXX in the PBE0 functional properly has a negligible effect on the results. For the G3-1 subset, use of the EXX boosts the accuracy of the PBE0 functional by 0.24 kcal/mol. The improvement of the PBE0-EXX over the PBE0-HFX further increases to 0.42 kcal/mol for the G3-3 subset containing the largest molecules. Thus, the proper EXX does enhance the performance of hybrid functionals, but the magnitude of the improvement is relatively small ($\sim 4\%$), as anticipated by Becke [15].

3.3 Percentage of the EXX in hybrid density functionals

The numerical difference between PBE0-HFX and PBE0-EXX depends on the percentage of the HFX (or EXX) in the functional. To study this dependence, we will introduce the $\text{PBE}\alpha$ hybrid density functional

$$E_{\text{XC}}^{\text{PBE}\alpha}[\rho] = \alpha E^{\text{EXX}}[\rho] + (1 - \alpha) E_{\text{X}}^{\text{PBE}}[\rho] + E_{\text{C}}^{\text{PBE}}[\rho]. \quad (3.17)$$

where α is a constant between 0 and 1. We computed $\text{PBE}\alpha$ -EXX and $\text{PBE}\alpha$ -HFX energies of C, Ne, Mg and Ar atoms and methanol (CH_3OH), cyclobutene (C_4H_6) and PCl_3 molecules for α from 0 to 1 with the increment 0.1 using the UGBS for the atoms and the cc-pVTZ basis set for the molecules. The differences in the energies, $\Delta E^{\text{PBE}\alpha} = E^{\text{PBE}\alpha-\text{EXX}} - E^{\text{PBE}\alpha-\text{HFX}}$, are plotted in Fig. 3.1. These points fit the parabola $\Delta E^{\text{PBE}\alpha}(\alpha) = k\alpha^2 + b\alpha$. The constant in this quadratic function is zero because $E^{\text{PBE}\alpha-\text{EXX}}$ and $E^{\text{PBE}\alpha-\text{HFX}}$ are identical when $\alpha = 0$.

The only two parts in the calculation that depend on α are the energy functional and the orbitals. The $\text{PBE}\alpha$ hybrid density functional (Eq. (3.17)) varies linearly with respect to α .

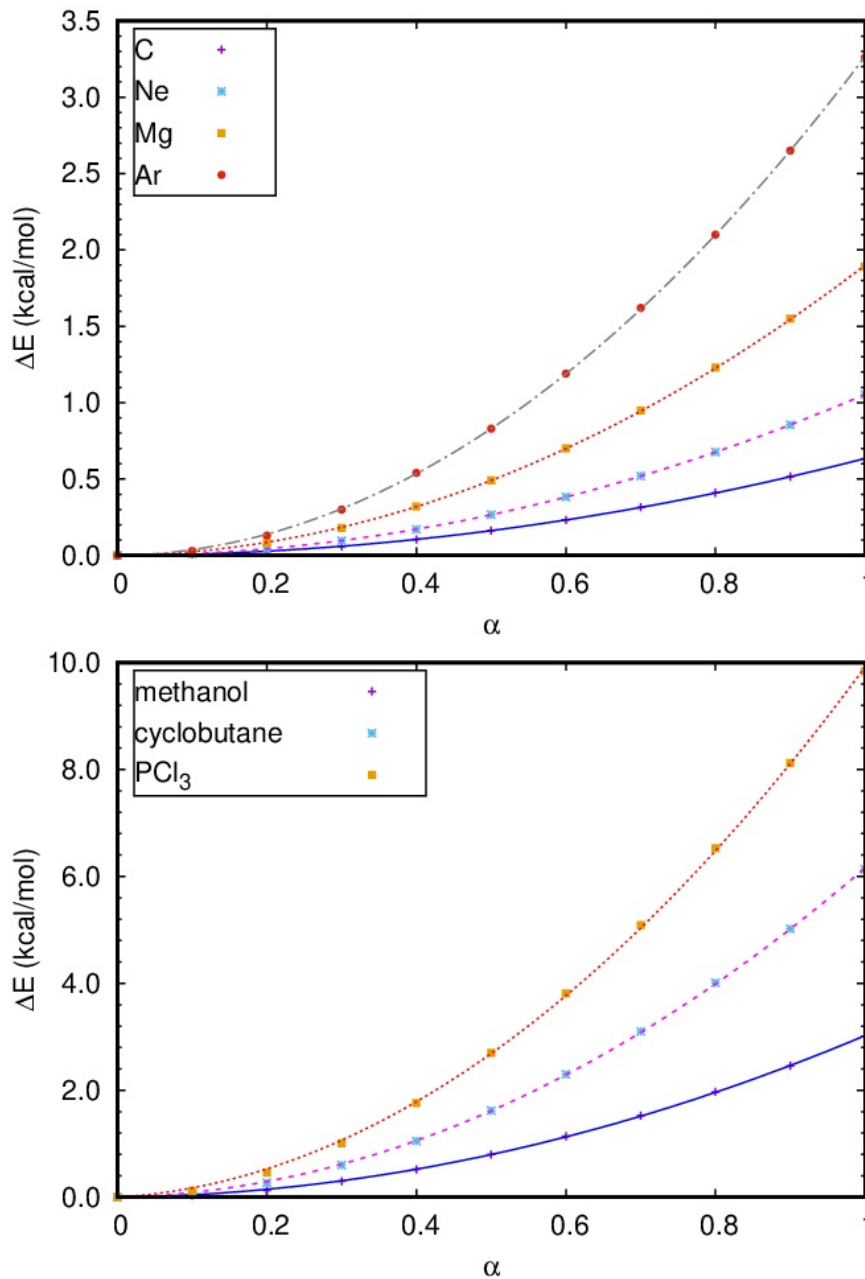


Figure 3.1: $\Delta E^{\text{PBE}\alpha}$ vs α for Be, Mg and Ar atoms (top) and methanol (CH_3OH), cyclobutene (C_4H_6) and PCl_3 molecules (bottom), where $\Delta E^{\text{PBE}\alpha} = E^{\text{PBE}\alpha\text{-EXX}} - E^{\text{PBE}\alpha\text{-HFX}}$ and α is the percentage of the EXX in the functional. The data points are fitted to $\Delta E^{\text{PBE}\alpha}(\alpha) = k\alpha^2 + b\alpha$. The fitted parameters are $k = 0.619 \pm 0.003$, $b = 0.016 \pm 0.003$ for C atom, $k = 1.042 \pm 0.002$, $b = 0.012 \pm 0.002$ for Ne atom, $k = 1.83 \pm 0.01$, $b = 0.06 \pm 0.01$ for Mg atom, $k = 3.21 \pm 0.01$, $b = 0.06 \pm 0.01$ for Ar atom, $k = 2.85 \pm 0.02$, $b = 0.17 \pm 0.02$ for methanol, $k = 5.85 \pm 0.05$, $b = 0.30 \pm 0.03$ for cyclobutene and $k = 9.1 \pm 0.1$, $b = 0.8 \pm 0.1$ for PCl_3 .

Hence the quadratic behavior of $\Delta E(\alpha)$ originates from the variation of orbitals. To verify this, we will introduce the exchange-only mix functional

$$E_X^{\text{mix}}[\rho] = \alpha E^{\text{EXX}}[\rho] + (1 - \alpha) E^{\text{HFX}}[\rho] \quad (3.18)$$

with the corresponding exchange potential

$$v_X^{\text{mix}}(\mathbf{r}) = \alpha v^{\text{EXX}}(\mathbf{r}) + (1 - \alpha) \hat{K}(\mathbf{r}), \quad (3.19)$$

where

$$v^{\text{EXX}}(\mathbf{r}) = \frac{\delta E^{\text{EXX}}[\rho]}{\delta \rho(\mathbf{r})}. \quad (3.20)$$

Here, both E^{EXX} and E^{EXX} uses the orbitals computed using v_X^{mix} , i.e., E^{EXX} and E^{EXX} are identical, hence E_X^{mix} is independent from α . This functional is implemented using the method introduced in Chapter 4.

We computed the exchange-only mix functional energies of Be, Mg and Ar atoms and PCl_3 , methanol (CH_3OH), cyclobutene (C_4H_6) and PCl_3 molecules using exchange-only mix functional for α from 0 to 1 with the increment 0.1 using the UGBS for the atoms and the cc-pVTZ basis set for the molecules. The energy differences, $\Delta E^{\text{mix}} = E^{\text{mix}} - E^{\text{HF}}$, are plotted in Fig. 3.2. The data points again fit the parabola $\Delta E^{\text{mix}}(\alpha) = k\alpha^2 + b\alpha$.

3.4 Summary

Using EXX in hybrid density functionals does improve their performance. The magnitude of the improvement increases with the size of the basis set used in the calculation, and the difference between using HFX and EXX in a hybrid density functional quadratically depends on the amount of EXX (or HFX) it has. In practice, the improvement is modest since we do

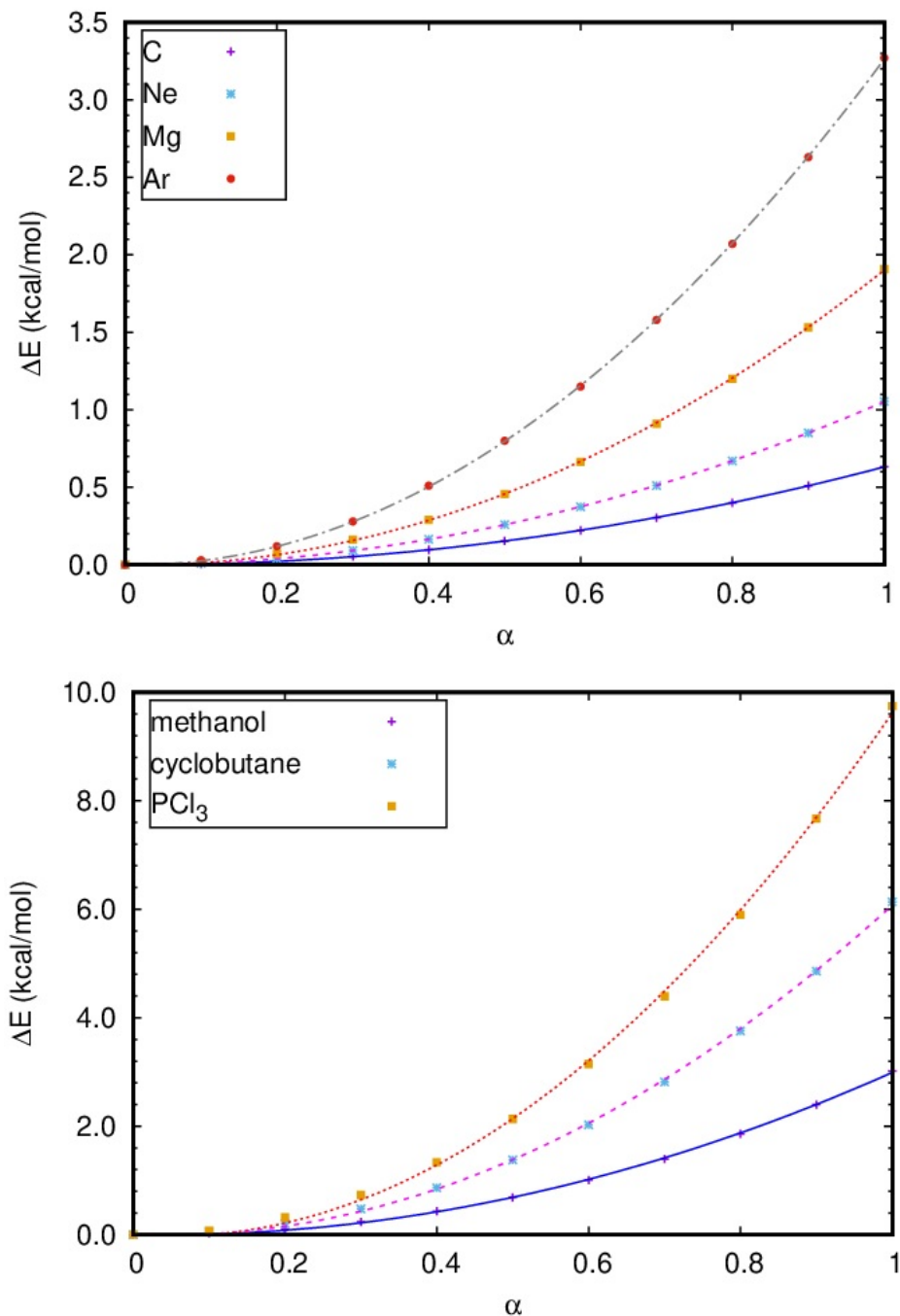


Figure 3.2: ΔE^{mix} vs α for Be, Mg and Ar atoms (top) and methanol (CH_3OH), cyclobutene (C_4H_6) and PCl_3 molecules (bottom), where $\Delta E^{\text{mix}} = E^{\text{mix}} - E^{\text{HF}}$. The data points are fitted to $\Delta E^{\text{mix}}(\alpha) = k\alpha^2 + b\alpha$. The fitted parameters are $k = 0.650 \pm 0.003$, $b = -0.019 \pm 0.002$ for C atom, $k = 1.068 \pm 0.002$, $b = -0.016 \pm 0.002$ for Ne atom, $k = 1.97 \pm 0.01$, $b = -0.07 \pm 0.01$ for Mg atom, $k = 3.34 \pm 0.01$, $b = -0.07 \pm 0.01$ for Ar atom, $k = 3.22 \pm 0.04$, $b = -0.23 \pm 0.04$ for methanol, $k = 6.6 \pm 0.1$, $b = -0.54 \pm 0.09$ for cyclobutene and $k = 10.7 \pm 0.1$, $b = -1.1 \pm 0.2$ for PCl_3

not use very large basis sets in daily calculations of medium-size molecules due to efficiency, and the typical amount of EXX (or HFX) in a hybrid density functional is 25%. Considering the extra computational cost for implementing the EXX properly, it is not worthwhile for us to modify the current implementations of hybrid density functionals to gain this improvement.

Chapter 4

The exact remainder exchange-correlation potential in the generalized Kohn–Sham DFT for hybrid density functional

In 1995, Seidl, Görling, Vogl and Majewski generalized Kohn–Sham DFT to describe interacting electrons using a single Slater determinant [23]. In this generalized scheme, the energy functional is partitioned as

$$E[\rho] = F_S[\rho] + E_R[\rho] + V[\rho], \quad (4.1)$$

where $F_S[\rho]$ is an energy functional that depends on the density implicitly via a single Slater determinant or its constituent orbitals. An example of $F_S[\rho]$ is the kinetic energy functional in the Kohn–Sham DFT. $V[\rho]$ is the same as the potential energy in Kohn–Sham DFT. $E_R[\rho]$ is the remainder. We can reproduce the Kohn–Sham formalism if we choose the remainder to be

$$E_R[\rho] = J[\rho] + E_{XC}[\rho]. \quad (4.2)$$

In the generalized Kohn–Sham DFT, using HFX in exact realizations of DFT is rationalized [23]. Observing the success of hybrid density functionals with HFX in Kohn–Sham DFT, Garrick *et al.* [24] implemented them into generalized Kohn–Sham DFT. Their idea is to

connect the real interacting system to a partially interacting system. In this scheme,

$$F_S[\rho] = \langle \Phi | \hat{T} + \alpha V_{ee} | \Phi \rangle, \quad (4.3)$$

where α is a constant between 0 and 1. If we minimize the energy with respect to the orbitals, we obtain

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \alpha \hat{K}(\mathbf{r}) + \alpha \hat{J}(\mathbf{r}) + v_R(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad (4.4)$$

where $v(\mathbf{r})$ is the electrostatic potential of the nuclei, $\hat{J}(\mathbf{r})$ is the Hartree potential, $\hat{K}(\mathbf{r})$ is the Hartree–Fock exchange operator, and

$$v_R(\mathbf{r}) = \frac{\delta E_R[\rho]}{\delta \rho(\mathbf{r})} \quad (4.5)$$

is the remainder potential. We may separate $E_R(\rho)$ into two parts

$$E_R(\rho) = (1 - \alpha)J[\rho] + E_{R,XC}^\alpha[\rho], \quad (4.6)$$

where $E_{R,XC}^\alpha[\rho]$ is the remainder exchange-correlation energy, and separate $v^R(\mathbf{r})$ accordingly as

$$v_R(\mathbf{r}) = (1 - \alpha)\hat{J}(\mathbf{r}) + v_{R,XC}^\alpha(\mathbf{r}), \quad (4.7)$$

where $v_{R,XC}^\alpha(\mathbf{r})$ is the remainder exchange-correlation potential. Then Eq. (4.4) becomes

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J}(\mathbf{r}) + \alpha \hat{K} + v_{R,XC}^\alpha(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (4.8)$$

And the density is constructed as

$$\rho^{\text{GKS}}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\phi_i(\mathbf{r})|^2, \quad (4.9)$$

$E_{\text{R,XC}}^\alpha[\rho]$ is unknown and needs to be approximated. Fortunately, it is possible to numerically generate $v_{\text{R,XC}}^\alpha(\mathbf{r})$. By studying the properties of $v_{\text{R,XC}}^\alpha(\mathbf{r})$, we can come up with accurate approximation to $E_{\text{R,XC}}^\alpha[\rho]$. Garrick *et al.* developed an inversion algorithm to generate $v_{\text{R,XC}}^\alpha(\mathbf{r})$ [24]. However, the resulting potentials have some unwanted noise. Here, we are going to introduce a better algorithm, which follows the idea of Ryabinkin *et al.* [18].

4.1 The mRKS-GKS method

The idea of our method is to derive two local energy balanced equations, and subtract one from the other. One of the local energy balanced equations is obtained from the generalized Kohn–Sham equation (Eq. (4.8)). If we multiply $\phi_i^*(\mathbf{r})$ from the left on both sides of Eq. (4.8), sum over all occupied orbitals for both sides of the equation, and then divide both sides by $\rho^{\text{GKS}}(\mathbf{r})$, we obtain

$$\frac{\tau_{\text{L}}^{\text{GKS}}(\mathbf{r})}{\rho^{\text{GKS}}(\mathbf{r})} + v(\mathbf{r}) + v_{\text{H}}^{\text{GKS}}(\mathbf{r}) + \alpha v_{\text{X}}^{\text{S}}(\mathbf{r}) + v_{\text{R,XC}}^\alpha(\mathbf{r}) = \bar{\epsilon}^{\text{GKS}}(\mathbf{r}) \quad (4.10)$$

where

$$\tau_{\text{L}}^{\text{GKS}}(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^{N/2} 2\phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) \quad (4.11)$$

is the generalized Kohn–Sham kinetic energy density,

$$v_{\text{X}}^{\text{S}}(\mathbf{r}) = \frac{2}{\rho^{\text{GKS}}(\mathbf{r})} \sum_{i=1}^{N/2} \phi_i^*(\mathbf{r}) \hat{K} \phi_i(\mathbf{r}) \quad (4.12)$$

is the Slater potential [20],

$$\bar{\epsilon}^{\text{GKS}}(\mathbf{r}) = \frac{2}{\rho^{\text{GKS}}(\mathbf{r})} \sum_{i=1}^{N/2} \epsilon_i |\phi_i(\mathbf{r})|^2 \quad (4.13)$$

is the average local generalized Kohn–Sham orbital energy [25].

The other local energy balanced equation is obtained from the N -electron Schrödinger

equation. Here, we are going to use the local energy balanced equation derived by Ryabinkin *et al.* [18]

$$\frac{\tau_L^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} + v(\mathbf{r}) + v_H^{\text{WF}}(\mathbf{r}) + v_{\text{XC}}^{\text{hole}}(\mathbf{r}) = \bar{\epsilon}^{\text{WF}}(\mathbf{r}). \quad (4.14)$$

Here, the *ab initio* density $\rho^{\text{WF}}(\mathbf{r})$ is given by

$$\rho^{\text{WF}}(\mathbf{r}) = \sum_j n_j |\chi_j(\mathbf{r})|^2, \quad (4.15)$$

where $\chi_j(\mathbf{r})$ are the natural orbitals, n_j are their corresponding occupation numbers,

$$\tau_L^{\text{WF}}(\mathbf{r}) = \sum_j n_j \chi_j(\mathbf{r})^* \frac{1}{2} \nabla^2 \chi_j(\mathbf{r}) \quad (4.16)$$

is the *ab initio* kinetic energy density, $v_{\text{XC}}^{\text{hole}}(\mathbf{r})$ is the exchange-correlation hole charge potential and

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) = \frac{1}{\rho^{\text{WF}}(\mathbf{r})} \sum_j \lambda_j |f_j(\mathbf{r})|^2 \quad (4.17)$$

is the *ab initio* average local electron energy, where $f_i(\mathbf{r})$ are the eigenfunctions of the generalized Fock operator and λ_i are their corresponding eigenvalues.

Before deriving the expression for $v_{\text{R,XC}}^\alpha(\mathbf{r})$, we first rewrite $\tau_L^{\text{GKS}}(\mathbf{r})$ and $\tau_L^{\text{WF}}(\mathbf{r})$ as

$$\tau_L^{\text{GKS}}(\mathbf{r}) = \tau_W^{\text{GKS}}(\mathbf{r}) + \tau_P^{\text{GKS}}(\mathbf{r}) - \frac{\nabla^2 \rho^{\text{GKS}}(\mathbf{r})}{4} \quad (4.18)$$

and

$$\tau_L^{\text{WF}}(\mathbf{r}) = \tau_W^{\text{WF}}(\mathbf{r}) + \tau_P^{\text{WF}}(\mathbf{r}) - \frac{\nabla^2 \rho^{\text{GKS}}(\mathbf{r})}{4}, \quad (4.19)$$

where

$$\tau_W(\mathbf{r}) = \frac{|\nabla \rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}, \quad (4.20)$$

$$\tau_P^{\text{GKS}}(\mathbf{r}) = \frac{1}{2\rho^{\text{GKS}}(\mathbf{r})} \sum_{i < j}^N |\phi_i(\mathbf{r}) \nabla \phi_j(\mathbf{r}) - \phi_j(\mathbf{r}) \nabla \phi_i(\mathbf{r})|^2, \quad (4.21)$$

$$\tau_{\text{P}}^{\text{WF}}(\mathbf{r}) = \frac{1}{2\rho^{\text{WF}}(\mathbf{r})} \sum_{i < j} n_i n_j |\chi_i(\mathbf{r}) \nabla \chi_j(\mathbf{r}) - \chi_j(\mathbf{r}) \nabla \chi_i(\mathbf{r})|^2 \quad (4.22)$$

Let us substitute Eq. (4.18) and (4.19) into Eq. (4.10) and (4.14) respectively, then subtract Eq. (4.10) from Eq. (4.14). After applying the complete basis limit condition $\rho^{\text{GKS}}(\mathbf{r}) = \rho^{\text{WF}}(\mathbf{r})$ and rearranging the terms, we have

$$v_{\text{R,XC}}^{\alpha}(\mathbf{r}) = v_{\text{XC}}^{\text{hole}}(\mathbf{r}) - \alpha v_{\text{X}}^{\text{S}}(\mathbf{r}) + \bar{\epsilon}^{\text{GKS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}) + \frac{\tau_{\text{P}}^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau_{\text{P}}^{\text{GKS}}(\mathbf{r})}{\rho^{\text{GKS}}(\mathbf{r})}, \quad (4.23)$$

the key equation of our method. This equation depends on the generalized Kohn–Sham orbitals, and hence will be solved self-consistently with Eq. (4.8). The procedure to generate the exact remainder exchange-correlation potential will be referred to as mRKS-GKS method.

We can use the mRKS-GKS method to implement the exchange-only mix functional introduced in Chapter 3 by taking the Hartree–Fock wave function as input. In this chapter, this method is used to generate the exact remainder exchange-correlation potential from the wave functions computed by highly accurate *ab initio* methods.

4.2 Results and discussion

We computed the exchange-correlation potentials of Be atom, Li^- , F^- and Li^+ . The results are shown in Figures 4.1 to 4.4. For Li^+ , the remainder exchange-correlation potential we obtained is zero when $\alpha = 1$. This is because that in practice, the density is separated into spin-up and spin-down parts, and each part is computed individually. Li^+ has 2 electrons, hence each spin density has only 1 electron, which means the electron-electron interaction should vanish in the calculation of each spin density. When there is only 1 electron, the Hartree potential cancels the Hartree–Fock exchange-correlation potential for $\alpha = 1$, leaves the remainder exchange-correlation potential being zero.

We compared our results with those computed using the inversion algorithm (Fig. 2 in Ref. 24). For Be atom and Li^+ , the potentials generated using these two methods agree with

each other. If we compare these potentials carefully, we can find that the potentials generated by the inversion algorithm diverge at $r = 0$, while our potentials do not. Meanwhile, for Be atom, the potential generated by the inversion algorithm has unwanted oscillation near $r = 0$ when $\alpha = 1$, while ours does not have unwanted oscillations. Therefore, our method is better than the existing inversion algorithm.

The agreement in the potentials of Be atom and Li^+ suggest that these two methods should yield the same result. However, for Li^- and F^- , there are discrepancies between the two potentials. To figure out why these discrepancies arises, we are going to use the so called scaled remainder exchange potentials [24]

$$\tilde{v}_{\text{R,X}}^{\alpha}(\mathbf{r}) \equiv \frac{v_{\text{R,XC}}^{\alpha}(\mathbf{r}) - v_{\text{R,XC}}^{\alpha=1}(\mathbf{r})}{1 - \alpha}. \quad (4.24)$$

Garrick *et al.* [24] have shown that the scaled remainder exchange potential is independent from α , and their results agree with this property. We computed the scaled remainder exchange potentials for Be atom, Li^- , F^- and Li^+ using our method and the results are shown in Figures 4.1 to 4.4. These figures shows that our $\tilde{v}_{\text{R,X}}^{\alpha}(\mathbf{r})$ are also independent from α . In addition, our scaled remainder exchange potentials match those computed using the inversion algorithm (Fig. 3 in in Ref. 24). This means that the discrepancies between the exact remainder exchange-correlation potentials generated by these two methods are due to errors that are independent from α , e.g., noise. There is no discrepancy in the remainder exchange potentials since the errors cancelled out during the subtraction.

The spikes around $r = 0.5 a_0$ in the exact remainder exchange-correlation potentials of Li^- and F^- generated using the inversion algorithm suggest that these potentials are contaminated by noise; however, we cannot conclude that the potentials computed using the inversion algorithm are incorrect as we are lack of convincing evidence. Nevertheless, Since the potentials generated by the inversion algorithm contains noise for Li^- and F^- , our method again outperforms the inversion algorithm.

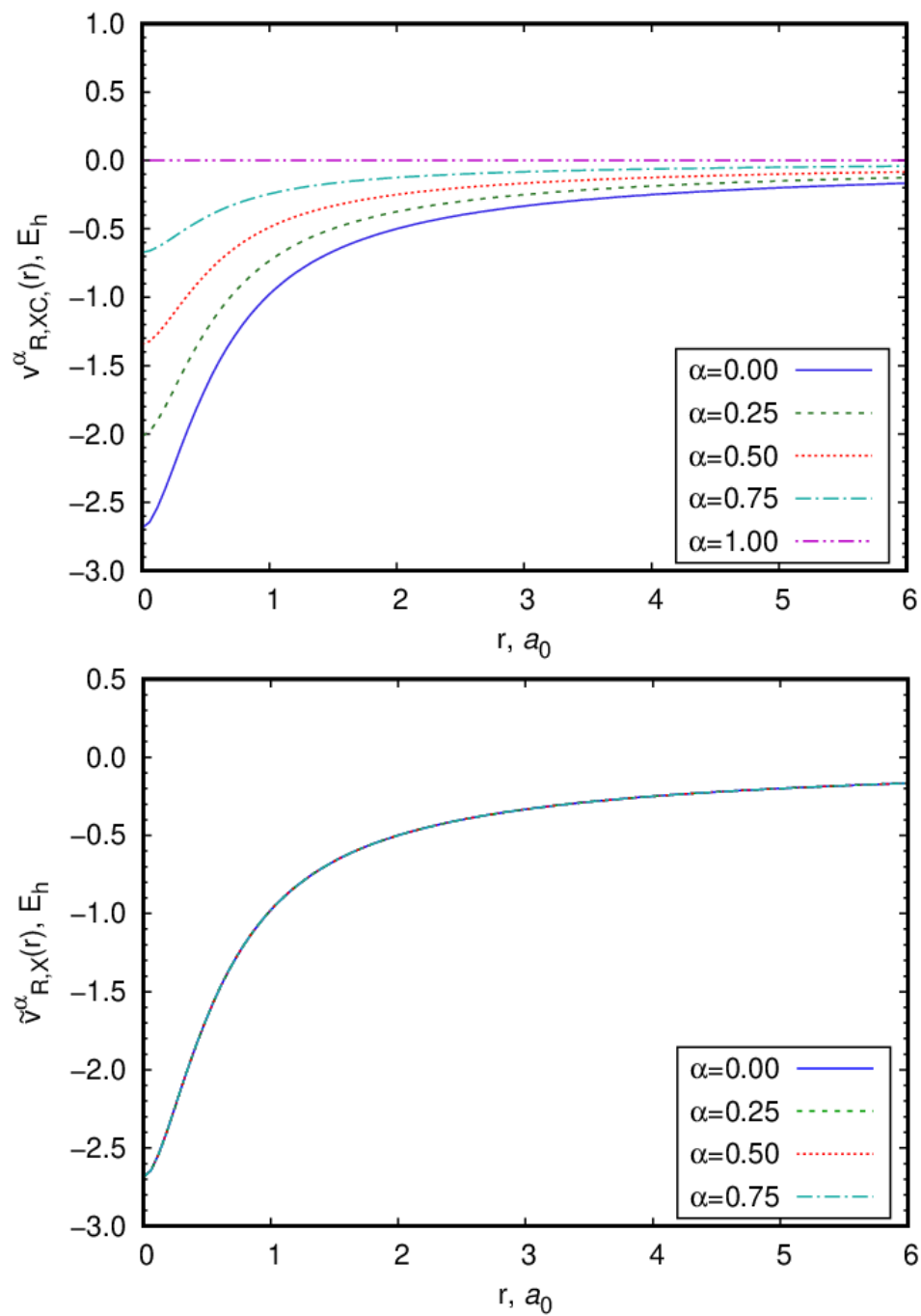


Figure 4.1: $v_{R,XC}^{\alpha}(\mathbf{r})$ and $\tilde{v}_{R,X}^{\alpha}(\mathbf{r})$ of Li^+ computed from CISD wave function using mRKS-GKS method with cc-pVQZ basis set.

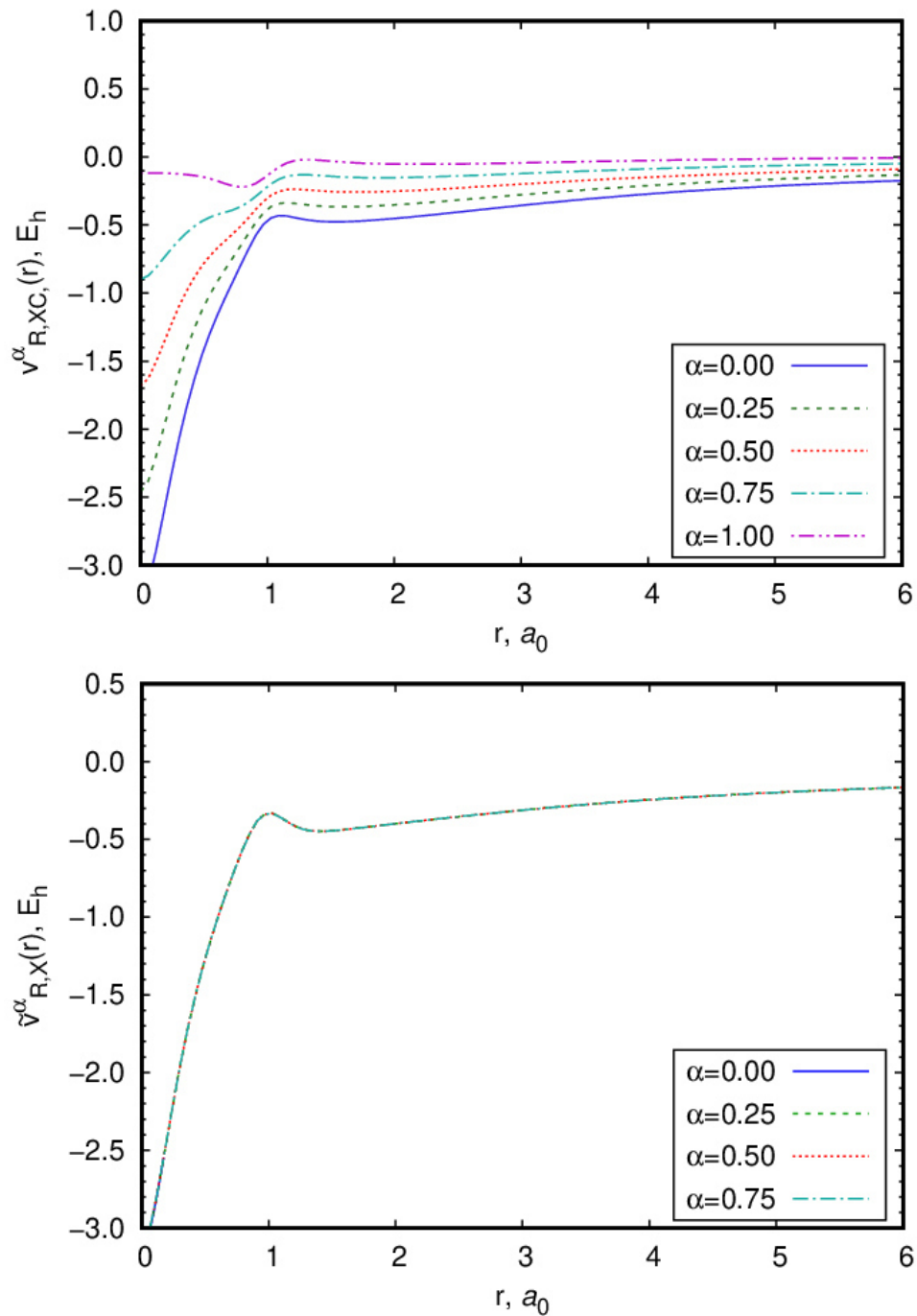


Figure 4.2: $v_{R,XC}^{\alpha}(\mathbf{r})$ and $\tilde{v}_{R,X}^{\alpha}(\mathbf{r})$ of Be atom computed from CASSCF(4,5) wave function using mRKS-GKS method with cc-pVQZ basis set.

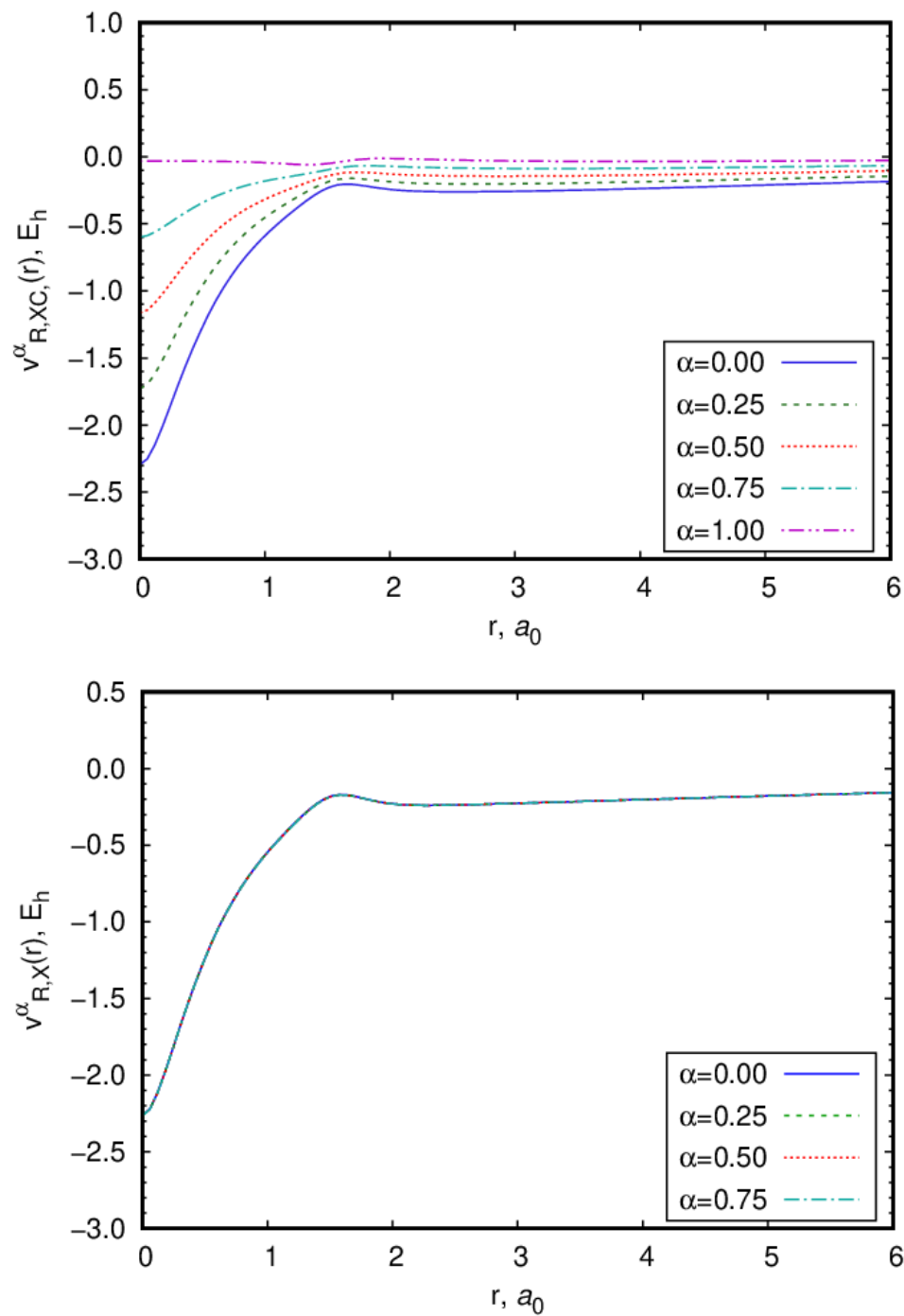


Figure 4.3: $v_{R,XC}^{\alpha}(\mathbf{r})$ and $\tilde{v}_{R,X}^{\alpha}(\mathbf{r})$ of Li^- computed from CASSCF(4,5) wave function using mRKS-GKS method with cc-pVQZ basis set.

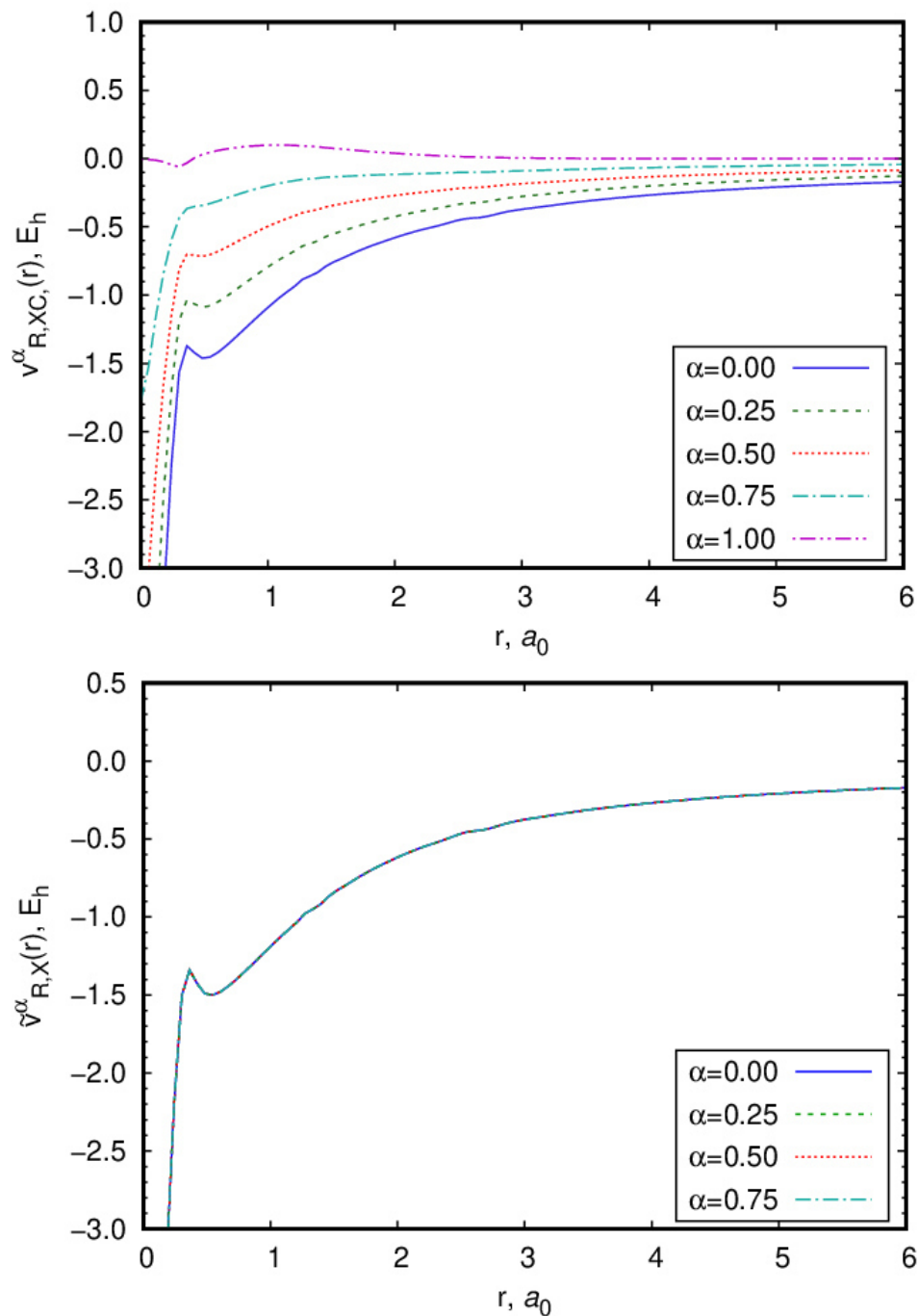


Figure 4.4: $v_{R,XC}^\alpha(\mathbf{r})$ and $\tilde{v}_{R,X}^\alpha(\mathbf{r})$ of F^- computed from CASSCF(10,8) wave function using mRKS-GKS method with cc-pVQZ basis set.

4.3 Summary

The mRKS-GKS method generates the exact remainder exchange-correlation potential from the wave function. This method outperforms the current existing method. Following the success of the conventional implementation hybrid density functionals, using HFX in DFT has become a popular topic in the last few years. With the exact remainder exchange-correlation potential generated correctly, studies based on these potentials can be carried on and eventually lead to high performance functionals.

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Appendix A

Standard enthalpies of formation of G3 test set

Table A.1: Standard enthalpies of formation (in kcal/mol) for the G3 molecules computed using 6-31G* basis set. All values are in kcal/mol

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
<i>G3-1 subset</i>					
LiH	33.3	40.2	6.9	40.2	6.9
BeH	81.7	75.5	-6.2	75.5	-6.2
CH	142.5	145.6	3.1	145.6	3.1
CH ₂ (³ B ₁)	93.7	91.9	-1.8	91.9	-1.8
CH ₂ (¹ A ₁)	102.8	111.2	8.4	111.2	8.4
CH ₃	35.0	35.2	0.2	35.2	0.2
CH ₄	-17.9	-16.2	1.7	-16.3	1.6
NH	85.2	87.0	1.8	87.0	1.8
NH ₂	45.1	51.0	5.9	51.0	5.9
NH ₃	-11.0	2.0	13.0	2.0	13.0
OH	9.4	16.2	6.8	16.1	6.7
H ₂ O	-57.8	-40.1	17.7	-40.1	17.7
FH	-65.1	-50.4	14.7	-50.4	14.7
SiH ₂ (¹ A ₁)	65.2	71.3	6.1	71.2	6.0
SiH ₂ (³ B ₁)	86.2	86.1	-0.1	86.1	-0.1
SiH ₃	47.9	51.6	3.7	51.5	3.6
SiH ₄	8.2	16.6	8.4	16.5	8.3
PH ₂	33.1	37.3	4.2	37.3	4.2
PH ₃	1.3	10.7	9.4	10.6	9.3
H ₂ S	-4.9	4.1	9.0	4.0	8.9
HCl	-22.1	-15.2	6.9	-15.2	6.9
Li ₂	51.6	57.4	5.8	57.4	5.8
LiF	-80.1	-69.8	10.3	-69.8	10.3
HC≡CH	54.2	60.6	6.4	60.6	6.4
CH ₂ =CH ₂	12.5	13.7	1.2	13.6	1.1
CH ₃ CH ₃	-20.1	-22.2	-2.1	-22.3	-2.2
CN	104.9	110.7	5.8	110.5	5.6
HCN	31.5	37.6	6.1	37.5	6.0
CO	-26.4	-20.0	6.4	-20.1	6.3

Continued on next page

Table A.1 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
CHO	10.0	10.7	0.7	10.7	0.7
CH ₂ O	-26.0	-23.2	2.8	-23.3	2.7
CH ₃ OH	-48.0	-40.1	7.9	-40.2	7.8
N ₂	0.0	9.7	9.7	9.6	9.6
N ₂ H ₄	22.8	35.8	13.0	35.7	12.9
NO	21.6	24.0	2.4	23.9	2.3
O ₂	0.0	-4.1	-4.1	-4.2	-4.2
H ₂ O ₂	-32.5	-17.8	14.7	-17.9	14.6
F ₂	0.0	-0.5	-0.5	-0.7	-0.7
CO ₂	-94.1	-93.2	0.9	-93.4	0.7
Na ₂	34.0	35.1	1.1	35.1	1.1
Si ₂	139.9	142.0	2.1	141.9	2.0
P ₂	34.3	47.9	13.6	47.8	13.5
S ₂	30.7	34.3	3.6	34.2	3.5
Cl ₂	0.0	7.0	7.0	6.9	6.9
NaCl	-43.6	-37.2	6.4	-37.2	6.4
SiO	-24.6	-8.0	16.6	-8.0	16.6
CS	66.9	74.7	7.8	74.6	7.7
SO	1.2	9.6	8.4	9.5	8.3
ClO	24.2	28.8	4.6	28.6	4.4
ClF	-13.2	-8.5	4.7	-8.7	4.5
Si ₂ H ₆	19.1	29.6	10.5	29.5	10.4
CH ₃ Cl	-19.6	-20.0	-0.4	-20.0	-0.4
CH ₃ SH	-5.5	-1.5	4.0	-1.6	3.9
HOCl	-17.8	-7.2	10.6	-7.3	10.5
SO ₂	-71.0	-39.7	31.3	-40.0	31.0
<i>G3-2 subset</i>					
BF ₃	-271.4	-273.2	-1.8	-273.4	-2.0
BCl ₃	-96.3	-101.3	-5.0	-101.5	-5.2
AlF ₃	-289.0	-268.8	20.2	-268.9	20.1
AlCl ₃	-139.7	-130.2	9.5	-130.3	9.4
CF ₄	-223.0	-235.9	-12.9	-236.3	-13.3
CCl ₄	-22.9	-20.0	2.9	-20.4	2.5
COS	-33.1	-32.8	0.3	-33.0	0.1
CS ₂	28.0	27.7	-0.3	27.5	-0.5
COF ₂	-149.1	-151.4	-2.3	-151.7	-2.6
SiF ₄	-386.0	-357.8	28.2	-358.0	28.0
SiCl ₄	-158.4	-140.6	17.8	-140.8	17.6
N ₂ O	19.6	21.0	1.4	20.7	1.1
NOCl	12.4	14.6	2.2	14.3	1.9
NF ₃	-31.6	-39.4	-7.8	-39.9	-8.3
PF ₃	-229.1	-206.8	22.3	-207.2	21.9
O ₃	34.1	42.7	8.6	42.3	8.2
F ₂ O	5.9	3.6	-2.3	3.1	-2.8
ClF ₃	-38.0	-26.5	11.5	-27.0	11.0
CF ₂ =CF ₂	-157.4	-176.1	-18.7	-176.6	-19.2
CCl ₂ =CCl ₂	-3.0	-8.2	-5.2	-8.7	-5.7
CF ₃ CN	-118.4	-128.6	-10.2	-129.1	-10.7
CH ₃ C≡CH (propyne)	44.2	44.4	0.2	44.3	0.1
CH ₂ =C=CH ₂ (allene)	45.5	41.8	-3.7	41.6	-3.9

Continued on next page

Table A.1 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
C ₃ H ₄ (cyclopropene)	66.2	61.5	-4.7	61.4	-4.8
CH ₃ CH=CH ₂ (propylene)	4.8	2.0	-2.8	1.9	-2.9
C ₃ H ₆ (cyclopropane)	12.7	5.2	-7.5	5.1	-7.6
C ₃ H ₈ (propane)	-25.0	-29.9	-4.9	-30.0	-5.0
C ₄ H ₆ (1,3-butadiene)	26.3	22.3	-4.0	22.0	-4.3
C ₄ H ₆ (2-butyne)	34.8	29.7	-5.1	29.5	-5.3
C ₄ H ₆ (methylene cyclopropane)	47.9	35.3	-12.6	35.1	-12.8
C ₄ H ₆ (bicyclobutane)	51.9	39.6	-12.3	39.5	-12.4
C ₄ H ₆ (cyclobutene)	37.4	28.1	-9.3	27.9	-9.5
C ₄ H ₈ (cyclobutane)	6.8	-5.2	-12.0	-5.3	-12.1
C ₄ H ₈ (isobutene)	-4.0	-9.7	-5.7	-9.9	-5.9
C ₄ H ₁₀ (butane)	-30.0	-37.5	-7.5	-37.7	-7.7
C ₄ H ₁₀ (isobutane)	-32.1	-38.6	-6.5	-38.7	-6.6
C ₅ H ₈ (spiropentane)	44.3	26.1	-18.2	25.9	-18.4
C ₆ H ₆ (benzene)	19.7	1.6	-18.1	1.4	-18.3
CH ₂ F ₂	-107.7	-108.5	-0.8	-108.7	-1.0
CHF ₃	-166.6	-172.5	-5.9	-172.8	-6.2
CH ₂ Cl ₂	-22.8	-23.1	-0.3	-23.2	-0.4
CHCl ₃	-24.7	-23.7	1.0	-24.0	0.7
CH ₃ NH ₂ (methylamine)	-5.5	0.9	6.4	0.8	6.3
CH ₃ CN (acetonitrile)	18.0	18.4	0.4	18.2	0.2
CH ₃ NO ₂ (nitromethane)	-17.8	-19.8	-2.0	-20.1	-2.3
CH ₃ ONO (methyl nitrite)	-15.9	-16.8	-0.9	-17.3	-1.4
CH ₃ SiH ₃ (methyl silane)	-7.0	1.1	8.1	1.0	8.0
HCOOH (formic acid)	-90.5	-85.1	5.4	-85.3	5.2
HCOOCH ₃ (methyl formate)	-85.0	-87.0	-2.0	-87.3	-2.3
CH ₃ CONH ₂ (acetamide)	-57.0	-54.8	2.2	-55.1	1.9
C ₂ H ₄ NH (aziridine)	30.2	27.8	-2.4	27.7	-2.5
(CN) ₂ (cyanogen)	73.3	76.2	2.9	75.9	2.6
(CH ₃) ₂ NH (dimethylamine)	-4.4	-3.7	0.7	-3.9	0.5
CH ₃ CH ₂ NH ₂ (ethylamine)	-11.3	-9.1	2.2	-9.3	2.0
CH ₂ =C=O (ketene)	-11.4	-13.5	-2.1	-13.6	-2.2
C ₂ H ₄ O (oxirane)	-12.6	-16.0	-3.4	-16.1	-3.5
CH ₃ CHO (acetaldehyde)	-39.7	-40.8	-1.1	-41.0	-1.3
HCOCHO (glyoxal)	-50.7	-51.4	-0.7	-51.7	-1.0
CH ₃ CH ₂ OH (ethanol)	-56.2	-51.2	5.0	-51.4	4.8
CH ₃ OCH ₃ (dimethyl ether)	-44.0	-44.2	-0.2	-44.4	-0.4
C ₂ H ₄ S (thiirane)	19.6	15.0	-4.6	14.9	-4.7
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-20.4	15.8	-20.8	15.4
C ₂ H ₅ SH (ethanethiol)	-11.1	-9.6	1.5	-9.7	1.4
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	-9.4	-0.5	-9.6	-0.7
CH ₂ =CHF (vinyl fluoride)	-33.2	-36.0	-2.8	-36.2	-3.0
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-30.0	-3.2	-30.2	-3.4
CH ₂ =CHCl (vinyl chloride)	8.9	3.9	-5.0	3.7	-5.2
CH ₂ =CHCN (acrylonitrile)	43.2	43.8	0.6	43.5	0.3
CH ₃ COCH ₃ (acetone)	-51.9	-56.0	-4.1	-56.3	-4.4
CH ₃ COOH (acetic acid)	-103.4	-101.0	2.4	-101.2	2.2
CH ₃ COF (acetyl fluoride)	-105.7	-109.7	-4.0	-110.0	-4.3
CH ₃ COCl (acetyl chloride)	-58.0	-61.1	-3.1	-61.4	-3.4
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-37.7	-6.2	-37.9	-6.4

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Table A.1 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-62.9	2.3	-63.2	2.0
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-55.2	-3.5	-55.5	-3.8
(CH ₃) ₃ N (trimethylamine)	-5.7	-10.0	-4.3	-10.3	-4.6
C ₄ H ₄ O (furan)	-8.3	-19.3	-11.0	-19.6	-11.3
C ₄ H ₄ S (thiophene)	27.5	20.2	-7.3	19.9	-7.6
C ₄ H ₅ N (pyrrole)	25.9	16.2	-9.7	16.0	-9.9
C ₅ H ₅ N (pyridine)	33.6	16.4	-17.2	16.1	-17.5
H ₂	0.0	5.6	5.6	5.6	5.6
SH	34.2	38.0	3.8	38.0	3.8
C≡CH (² A', C _s)	135.1	138.1	3.0	138.0	2.9
CH=CH ₂ (² A', C _s)	71.6	69.2	-2.4	69.1	-2.5
CH ₃ CO (² A', C _s)	-2.4	-5.8	-3.4	-6.0	-3.6
CH ₂ OH (² A, C ₁)	-4.1	1.0	5.1	0.9	5.0
CH ₃ O (² A', C _s)	4.1	1.9	-2.2	1.7	-2.4
CH ₃ CH ₂ O (² A'', C _s)	-3.7	-10.4	-6.7	-10.7	-7.0
CH ₃ S (² A', C _s)	29.8	27.3	-2.5	27.1	-2.7
CH ₃ CH ₂ (² A', C _s)	28.9	24.6	-4.3	24.5	-4.4
(CH ₃) ₂ CH (² A', C _s)	21.5	13.0	-8.5	12.9	-8.6
(CH ₃) ₃ C (<i>t</i> -butyl radical, C _{3v})	12.3	1.3	-11.0	1.1	-11.2
NO ₂	7.9	5.4	-2.5	5.1	-2.8
<i>G3-3 subset</i>					
CH ₂ =C=CHCH ₃ (1,2-butadiene)	38.8	31.6	-7.2	31.4	-7.4
CH ₂ =CH-C(CH ₃)=CH ₂ (isoprene)	18.0	11.4	-6.6	11.1	-6.9
C ₅ H ₁₀ (cyclopentane)	-18.3	-32.3	-14.0	-32.5	-14.2
C ₅ H ₁₂ (<i>n</i> -pentane)	-35.1	-45.1	-10.0	-45.4	-10.3
C(CH ₃) ₄ (neopentane)	-40.2	-47.5	-7.3	-47.7	-7.5
C ₆ H ₈ (1,3-cyclohexadiene)	25.4	11.1	-14.3	10.8	-14.6
C ₆ H ₈ (1,4-cyclohexadiene)	25.0	11.2	-13.8	10.8	-14.2
C ₆ H ₁₂ (cyclohexane)	-29.5	-45.4	-15.9	-45.8	-16.3
C ₆ H ₁₄ (<i>n</i> -hexane)	-39.9	-52.7	-12.8	-53.0	-13.1
C ₆ H ₁₄ (3-methyl pentane)	-41.1	-52.0	-10.9	-52.3	-11.2
C ₆ H ₅ CH ₃ (toluene)	12.0	-9.0	-21.0	-9.3	-21.3
C ₇ H ₁₆ (<i>n</i> -heptane)	-44.9	-60.3	-15.4	-60.7	-15.8
C ₈ H ₈ (1,3,5,7-cyclooctatetraene)	70.7	53.8	-16.9	53.2	-17.5
C ₈ H ₁₈ (<i>n</i> -octane)	-49.9	-67.9	-18.0	-68.4	-18.5
C ₁₀ H ₈ (naphthalene)	35.9	0.2	-35.7	-0.3	-36.2
C ₁₀ H ₈ (azulene)	69.1	34.9	-34.2	34.4	-34.7
CH ₃ COOCH ₃ (methyl acetate)	-98.4	-102.4	-4.0	-102.8	-4.4
(CH ₃) ₃ COH (<i>t</i> -butanol)	-74.7	-73.9	0.8	-74.2	0.5
C ₆ H ₅ NH ₂ (aniline)	20.8	5.6	-15.2	5.3	-15.5
C ₆ H ₅ OH (phenol)	-23.0	-36.5	-13.5	-36.9	-13.9
CH ₂ =CH-O-CH=CH ₂ (divinyl ether)	-3.3	-7.1	-3.8	-7.4	-4.1
C ₄ H ₈ O (tetrahydrofuran)	-44.0	-53.3	-9.3	-53.7	-9.7
C ₅ H ₈ O (cyclopentanone)	-45.9	-60.7	-14.8	-61.1	-15.2
C ₆ H ₄ O ₂ (1,4-benzoquinone)	-29.4	-44.6	-15.2	-45.4	-16.0
C ₄ H ₄ N ₂ (pyrimidine)	46.8	29.4	-17.4	29.0	-17.8
(CH ₃) ₂ SO ₂ (dimethyl sulfone)	-89.2	-58.1	31.1	-58.5	30.7
C ₆ H ₅ Cl (chlorobenzene)	12.4	-7.4	-19.8	-7.8	-20.2
NC-CH ₂ CH ₂ -CN (succinonitrile)	50.1	47.9	-2.2	47.5	-2.6
C ₄ H ₄ N ₂ (pyrazine)	46.9	33.6	-13.3	33.3	-13.6

Continued on next page

Table A.1 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
CH ₃ COC≡CH (acetyl acetylene)	15.6	15.2	-0.4	14.9	-0.7
CH ₃ -CH=CH-CHO (crotonaldehyde)	-24.0	-31.7	-7.7	-32.1	-8.1
(CH ₃ CO) ₂ O (acetic anhydride)	-136.8	-145.8	-9.0	-146.4	-9.6
C ₄ H ₆ S (2,5-dihydrothiophene)	20.8	11.7	-9.1	11.4	-9.4
CH ₃ CH(CH ₃)CN (2-methyl propanenitrile)	5.6	2.8	-2.8	2.5	-3.1
CH ₃ -CO-CH ₂ CH ₃ (methyl ethyl ketone)	-57.1	-64.4	-7.3	-64.7	-7.6
(CH ₃) ₂ CH-CHO (isobutyraldehyde)	-51.6	-56.4	-4.8	-56.7	-5.1
C ₄ H ₈ O ₂ (1,4-dioxane)	-75.5	-84.2	-8.7	-84.7	-9.2
C ₄ H ₈ S (tetrahydrothiophene)	-8.2	-17.2	-9.0	-17.5	-9.3
(CH ₃) ₃ C-Cl (<i>t</i> -butyl chloride)	-43.5	-50.4	-6.9	-50.6	-7.1
CH ₃ CH ₂ CH ₂ CH ₂ Cl (<i>n</i> -butyl chloride)	-37.0	-45.3	-8.3	-45.5	-8.5
C ₄ H ₈ NH (pyrrolidine)	-0.8	-9.3	-8.5	-9.6	-8.8
CH ₃ CH ₂ CH(NO ₂)CH ₃ (2-nitrobutane)	-39.1	-48.2	-9.1	-48.7	-9.6
CH ₃ CH ₂ OCH ₂ CH ₃ (diethyl ether)	-60.3	-66.2	-5.9	-66.5	-6.2
CH ₃ -CH(OCH ₃) ₂ (1,1-dimethoxy ethane)	-93.1	-97.4	-4.3	-97.9	-4.8
(CH ₃) ₃ C-SH (<i>t</i> -butanethiol)	-26.2	-28.1	-1.9	-28.4	-2.2
(CH ₃ CH ₂ S) ₂ (diethyl disulfide)	-17.9	-18.3	-0.4	-18.8	-0.9
(CH ₃) ₃ C-NH ₂ (<i>t</i> -butylamine)	-28.9	-29.0	-0.1	-29.3	-0.4
Si(CH ₃) ₄ (tetramethyl silane)	-55.7	-46.2	9.5	-46.4	9.3
C ₅ H ₆ S (2-methyl thiophene)	20.0	9.2	-10.8	8.9	-11.1
C ₅ H ₇ N (<i>N</i> -methyl pyrrole)	24.6	10.4	-14.2	10.1	-14.5
C ₅ H ₁₀ O (tetrahydropyran)	-53.4	-65.6	-12.2	-66.1	-12.7
C ₂ H ₅ COC ₂ H ₅ (diethyl ketone)	-61.6	-72.5	-10.9	-72.9	-11.3
CH ₃ COOCH(CH ₃) ₂ (isopropyl acetate)	-115.1	-124.3	-9.2	-124.8	-9.7
C ₅ H ₁₀ S (tetrahydrothiopyran)	-15.2	-26.8	-11.6	-27.2	-12.0
C ₅ H ₁₀ NH (piperidine)	-11.3	-22.4	-11.1	-22.7	-11.4
(CH ₃) ₃ COCH ₃ (<i>t</i> -butyl methyl ether)	-67.8	-73.9	-6.1	-74.3	-6.5
C ₆ H ₄ F ₂ (1,3-difluorobenzene)	-73.9	-99.7	-25.8	-100.2	-26.3
C ₆ H ₄ F ₂ (1,4-difluorobenzene)	-73.3	-99.0	-25.7	-99.4	-26.1
C ₆ H ₅ F (fluorobenzene)	-27.7	-49.3	-21.6	-49.7	-22.0
(CH ₃) ₂ CHOCH(CH ₃) ₂ (diisopropyl ether)	-76.3	-86.2	-9.9	-86.6	-10.3
PF ₅	-381.1	-351.2	29.9	-351.6	29.5
SF ₆	-291.7	-266.9	24.8	-267.6	24.1
P ₄	14.1	37.0	22.9	36.7	22.6
SO ₃	-94.6	-52.0	42.6	-52.5	42.1
SCl ₂	-4.2	7.8	12.0	7.6	11.8
POCl ₃	-133.8	-103.1	30.7	-103.4	30.4
PCl ₅	-86.1	-58.0	28.1	-58.5	27.6
SO ₂ Cl ₂	-84.8	-41.6	43.2	-42.1	42.7
PCl ₃	-69.0	-52.1	16.9	-52.4	16.6
S ₂ Cl ₂	-4.0	9.9	13.9	9.4	13.4
SiCl ₂ (¹ A ₁)	-40.3	-31.2	9.1	-31.3	9.0
CF ₃ Cl	-169.5	-178.8	-9.3	-179.2	-9.7
C ₂ F ₆	-321.3	-343.0	-21.7	-343.7	-22.4
CF ₃	-111.3	-123.4	-12.1	-123.7	-12.4
C ₆ H ₅ (phenyl radical)	81.2	58.7	-22.5	58.5	-22.7

Table A.2: Standard enthalpies of formation (in kcal/mol) for the G3 molecules computed using 6-311+G(2d,p) basis set. All values are in kcal/mol

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
<i>G3-1 subset</i>					
LiH	33.3	38.7	5.4	38.7	5.4
BeH	81.7	75.9	-5.8	75.9	-5.8
CH	142.5	143.9	1.4	143.9	1.4
CH ₂ (³ B ₁)	93.7	91.0	-2.7	91.0	-2.7
CH ₂ (¹ A ₁)	102.8	108.1	5.3	108.0	5.2
CH ₃	35.0	35.0	0.0	34.9	-0.1
CH ₄	-17.9	-14.5	3.4	-14.5	3.4
NH	85.2	84.3	-0.9	84.2	-1.0
NH ₂	45.1	45.3	0.2	45.2	0.1
NH ₃	-11.0	-6.2	4.8	-6.3	4.7
OH	9.4	11.1	1.7	11.0	1.6
H ₂ O	-57.8	-50.6	7.2	-50.6	7.2
FH	-65.1	-60.0	5.1	-60.0	5.1
SiH ₂ (¹ A ₁)	65.2	70.1	4.9	70.1	4.9
SiH ₂ (³ B ₁)	86.2	85.3	-0.9	85.3	-0.9
SiH ₃	47.9	50.7	2.8	50.6	2.7
SiH ₄	8.2	15.8	7.6	15.7	7.5
PH ₂	33.1	33.9	0.8	33.9	0.8
PH ₃	1.3	6.8	5.5	6.7	5.4
H ₂ S	-4.9	-1.1	3.8	-1.2	3.7
HCl	-22.1	-20.0	2.1	-20.0	2.1
Li ₂	51.6	56.5	4.9	56.5	4.9
LiF	-80.1	-74.6	5.5	-74.6	5.5
HC≡CH	54.2	57.5	3.3	57.4	3.2
CH ₂ =CH ₂	12.5	14.0	1.5	13.9	1.4
CH ₃ CH ₃	-20.1	-18.3	1.8	-18.4	1.7
CN	104.9	109.5	4.6	109.4	4.5
HCN	31.5	35.2	3.7	35.1	3.6
CO	-26.4	-21.2	5.2	-21.3	5.1
CHO	10.0	9.7	-0.3	9.6	-0.4
CH ₂ O	-26.0	-23.1	2.9	-23.3	2.7
CH ₃ OH	-48.0	-43.3	4.7	-43.4	4.6
N ₂	0.0	5.6	5.6	5.5	5.5
N ₂ H ₄	22.8	26.0	3.2	25.9	3.1
NO	21.6	23.4	1.8	23.3	1.7
O ₂	0.0	-2.3	-2.3	-2.4	-2.4
H ₂ O ₂	-32.5	-24.9	7.6	-25.0	7.5
F ₂	0.0	5.2	5.2	5.1	5.1
CO ₂	-94.1	-93.5	0.6	-93.7	0.4
Na ₂	34.0	35.1	1.1	35.0	1.0
Si ₂	139.9	138.5	-1.4	138.4	-1.5
P ₂	34.3	42.1	7.8	42.0	7.7
S ₂	30.7	28.9	-1.8	28.8	-1.9
Cl ₂	0.0	1.0	1.0	0.9	0.9
NaCl	-43.6	-40.1	3.5	-40.1	3.5
SiO	-24.6	-12.5	12.1	-12.5	12.1

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Table A.2 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
CS	66.9	71.8	4.9	71.7	4.8
SO	1.2	4.6	3.4	4.5	3.3
ClO	24.2	26.1	1.9	25.9	1.7
ClF	-13.2	-8.6	4.6	-8.8	4.4
Si ₂ H ₆	19.1	28.8	9.7	28.6	9.5
CH ₃ Cl	-19.6	-19.4	0.2	-19.5	0.1
CH ₃ SH	-5.5	-2.8	2.7	-2.9	2.6
HOCl	-17.8	-12.5	5.3	-12.7	5.1
SO ₂	-71.0	-52.2	18.8	-52.5	18.5
<i>G3-2 subset</i>					
BF ₃	-271.4	-263.9	7.5	-264.1	7.3
BCl ₃	-96.3	-102.7	-6.4	-102.9	-6.6
AlF ₃	-289.0	-268.1	20.9	-268.2	20.8
AlCl ₃	-139.7	-136.4	3.3	-136.5	3.2
CF ₄	-223.0	-219.0	4.0	-219.4	3.6
CCl ₄	-22.9	-25.5	-2.6	-26.0	-3.1
COS	-33.1	-34.5	-1.4	-34.7	-1.6
CS ₂	28.0	26.2	-1.8	26.0	-2.0
COF ₂	-149.1	-143.8	5.3	-144.1	5.0
SiF ₄	-386.0	-352.5	33.5	-352.7	33.3
SiCl ₄	-158.4	-150.9	7.5	-151.1	7.3
N ₂ O	19.6	19.0	-0.6	18.7	-0.9
NOCl	12.4	13.1	0.7	12.7	0.3
NF ₃	-31.6	-31.0	0.6	-31.7	-0.1
PF ₃	-229.1	-205.8	23.3	-206.2	22.9
O ₃	34.1	44.0	9.9	43.6	9.5
F ₂ O	5.9	10.1	4.2	9.6	3.7
ClF ₃	-38.0	-29.7	8.3	-30.2	7.8
CF ₂ =CF ₂	-157.4	-164.2	-6.8	-164.7	-7.3
CCl ₂ =CCl ₂	-3.0	-12.2	-9.2	-12.7	-9.7
CF ₃ CN	-118.4	-117.0	1.4	-117.5	0.9
CH ₃ C≡CH (propyne)	44.2	44.0	-0.2	43.9	-0.3
CH ₂ =C=CH ₂ (allene)	45.5	42.1	-3.4	41.9	-3.6
C ₃ H ₄ (cyclopropene)	66.2	63.7	-2.5	63.6	-2.6
CH ₃ CH=CH ₂ (propylene)	4.8	4.6	-0.2	4.4	-0.4
C ₃ H ₆ (cyclopropane)	12.7	9.6	-3.1	9.5	-3.2
C ₃ H ₈ (propane)	-25.0	-24.0	1.0	-24.2	0.8
C ₄ H ₆ (1,3-butadiene)	26.3	24.3	-2.0	24.0	-2.3
C ₄ H ₆ (2-butyne)	34.8	32.3	-2.5	32.0	-2.8
C ₄ H ₆ (methylene cyclopropane)	47.9	39.5	-8.4	39.2	-8.7
C ₄ H ₆ (bicyclobutane)	51.9	45.5	-6.4	45.2	-6.7
C ₄ H ₆ (cyclobutene)	37.4	32.8	-4.6	32.6	-4.8
C ₄ H ₈ (cyclobutane)	6.8	2.3	-4.5	2.0	-4.8
C ₄ H ₈ (isobutene)	-4.0	-4.8	-0.8	-5.1	-1.1
C ₄ H ₁₀ (butane)	-30.0	-29.6	0.4	-29.9	0.1
C ₄ H ₁₀ (isobutane)	-32.1	-30.7	1.4	-31.0	1.1
C ₅ H ₈ (spiropentane)	44.3	34.2	-10.1	33.9	-10.4
C ₆ H ₆ (benzene)	19.7	6.9	-12.8	6.6	-13.1
CH ₂ F ₂	-107.7	-104.8	2.9	-105.0	2.7
CHF ₃	-166.6	-163.0	3.6	-163.3	3.3

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Table A.2 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
CH ₂ Cl ₂	-22.8	-24.3	-1.5	-24.6	-1.8
CHCl ₃	-24.7	-27.0	-2.3	-27.4	-2.7
CH ₃ NH ₂ (methylamine)	-5.5	-2.4	3.1	-2.5	3.0
CH ₃ CN (acetonitrile)	18.0	18.5	0.5	18.3	0.3
CH ₃ NO ₂ (nitromethane)	-17.8	-19.1	-1.3	-19.5	-1.7
CH ₃ ONO (methyl nitrite)	-15.9	-13.3	2.6	-13.8	2.1
CH ₃ SiH ₃ (methyl silane)	-7.0	1.5	8.5	1.3	8.3
HCOOH (formic acid)	-90.5	-87.4	3.1	-87.7	2.8
HCOOCH ₃ (methyl formate)	-85.0	-83.2	1.8	-83.6	1.4
CH ₃ CONH ₂ (acetamide)	-57.0	-57.0	0.0	-57.3	-0.3
C ₂ H ₄ NH (aziridine)	30.2	28.1	-2.1	27.9	-2.3
(CN) ₂ (cyanogen)	73.3	74.8	1.5	74.4	1.1
(CH ₃) ₂ NH (dimethylamine)	-4.4	-2.3	2.1	-2.5	1.9
CH ₃ CH ₂ NH ₂ (ethylamine)	-11.3	-10.0	1.3	-10.2	1.1
CH ₂ =C=O (ketene)	-11.4	-14.1	-2.7	-14.3	-2.9
C ₂ H ₄ O (oxirane)	-12.6	-12.9	-0.3	-13.1	-0.5
CH ₃ CHO (acetaldehyde)	-39.7	-38.8	0.9	-39.1	0.6
HCOCHO (glyoxal)	-50.7	-49.9	0.8	-50.2	0.5
CH ₃ CH ₂ OH (ethanol)	-56.2	-52.3	3.9	-52.6	3.6
CH ₃ OCH ₃ (dimethyl ether)	-44.0	-40.2	3.8	-40.5	3.5
C ₂ H ₄ S (thiirane)	19.6	17.0	-2.6	16.8	-2.8
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-26.3	9.9	-26.7	9.5
C ₂ H ₅ SH (ethanethiol)	-11.1	-8.8	2.3	-9.1	2.0
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	-6.9	2.0	-7.1	1.8
CH ₂ =CHF (vinyl fluoride)	-33.2	-33.8	-0.6	-34.0	-0.8
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-27.4	-0.6	-27.6	-0.8
CH ₂ =CHCl (vinyl chloride)	8.9	3.6	-5.3	3.4	-5.5
CH ₂ =CHCN (acrylonitrile)	43.2	43.8	0.6	43.5	0.3
CH ₃ COCH ₃ (acetone)	-51.9	-52.1	-0.2	-52.4	-0.5
CH ₃ COOH (acetic acid)	-103.4	-101.5	1.9	-101.8	1.6
CH ₃ COF (acetyl fluoride)	-105.7	-105.0	0.7	-105.4	0.3
CH ₃ COCl (acetyl chloride)	-58.0	-60.4	-2.4	-60.8	-2.8
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-33.0	-1.5	-33.3	-1.8
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-61.7	3.5	-62.0	3.2
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-49.2	2.5	-49.6	2.1
(CH ₃) ₃ N (trimethylamine)	-5.7	-4.2	1.5	-4.5	1.2
C ₄ H ₄ O (furan)	-8.3	-15.2	-6.9	-15.5	-7.2
C ₄ H ₄ S (thiophene)	27.5	20.5	-7.0	20.2	-7.3
C ₄ H ₅ N (pyrrole)	25.9	16.6	-9.3	16.3	-9.6
C ₅ H ₅ N (pyridine)	33.6	20.7	-12.9	20.3	-13.3
H ₂	0.0	5.4	5.4	5.4	5.4
SH	34.2	35.1	0.9	35.1	0.9
C≡CH (² A', C _s)	135.1	136.0	0.9	135.9	0.8
CH=CH ₂ (² A', C _s)	71.6	68.5	-3.1	68.4	-3.2
CH ₃ CO (² A', C _s)	-2.4	-5.0	-2.6	-5.2	-2.8
CH ₂ OH (² A, C ₁)	-4.1	-3.2	0.9	-3.3	0.8
CH ₃ O (² A', C _s)	4.1	2.9	-1.2	2.6	-1.5
CH ₃ CH ₂ O (² A'', C _s)	-3.7	-7.1	-3.4	-7.4	-3.7
CH ₃ S (² A', C _s)	29.8	28.3	-1.5	28.2	-1.6
CH ₃ CH ₂ (² A', C _s)	28.9	26.6	-2.3	26.5	-2.4

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Table A.2 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
$(\text{CH}_3)_2\text{CH}$ ($^2A'$, C_s)	21.5	17.4	-4.1	17.2	-4.3
$(\text{CH}_3)_3\text{C}$ (<i>t</i> -butyl radical, C_{3v})	12.3	8.0	-4.3	7.7	-4.6
NO_2	7.9	5.2	-2.7	4.9	-3.0
<i>G3-3 subset</i>					
$\text{CH}_2=\text{C}=\text{CHCH}_3$ (1,2-butadiene)	38.8	34.4	-4.4	34.1	-4.7
$\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$ (isoprene)	18.0	15.6	-2.4	15.2	-2.8
C_5H_{10} (cyclopentane)	-18.3	-22.9	-4.6	-23.3	-5.0
C_5H_{12} (<i>n</i> -pentane)	-35.1	-35.2	-0.1	-35.5	-0.4
$\text{C}(\text{CH}_3)_4$ (neopentane)	-40.2	-37.6	2.6	-38.0	2.2
C_6H_8 (1,3-cyclohexadiene)	25.4	17.5	-7.9	17.0	-8.4
C_6H_8 (1,4-cyclohexadiene)	25.0	17.0	-8.0	16.6	-8.4
C_6H_{12} (cyclohexane)	-29.5	-33.4	-3.9	-33.9	-4.4
C_6H_{14} (<i>n</i> -hexane)	-39.9	-40.7	-0.8	-41.2	-1.3
C_6H_{14} (3-methyl pentane)	-41.1	-40.0	1.1	-40.5	0.6
$\text{C}_6\text{H}_5\text{CH}_3$ (toluene)	12.0	-1.5	-13.5	-1.9	-13.9
C_7H_{16} (<i>n</i> -heptane)	-44.9	-46.3	-1.4	-46.8	-1.9
C_8H_8 (1,3,5,7-cyclooctatetraene)	70.7	59.4	-11.3	58.7	-12.0
C_8H_{18} (<i>n</i> -octane)	-49.9	-51.9	-2.0	-52.5	-2.6
C_{10}H_8 (naphthalene)	35.9	10.2	-25.7	9.7	-26.2
C_{10}H_8 (azulene)	69.1	44.6	-24.5	44.0	-25.1
$\text{CH}_3\text{COOCH}_3$ (methyl acetate)	-98.4	-96.8	1.6	-97.2	1.2
$(\text{CH}_3)_3\text{COH}$ (<i>t</i> -butanol)	-74.7	-70.4	4.3	-70.8	3.9
$\text{C}_6\text{H}_5\text{NH}_2$ (aniline)	20.8	6.7	-14.1	6.2	-14.6
$\text{C}_6\text{H}_5\text{OH}$ (phenol)	-23.0	-34.4	-11.4	-34.8	-11.8
$\text{CH}_2=\text{CH}-\text{O}-\text{CH}=\text{CH}_2$ (divinyl ether)	-3.3	-4.4	-1.1	-4.8	-1.5
$\text{C}_4\text{H}_8\text{O}$ (tetrahydrofuran)	-44.0	-45.8	-1.8	-46.2	-2.2
$\text{C}_5\text{H}_8\text{O}$ (cyclopentanone)	-45.9	-52.8	-6.9	-53.3	-7.4
$\text{C}_6\text{H}_4\text{O}_2$ (1,4-benzoquinone)	-29.4	-39.0	-9.6	-39.8	-10.4
$\text{C}_4\text{H}_4\text{N}_2$ (pyrimidine)	46.8	32.3	-14.5	31.9	-14.9
$(\text{CH}_3)_2\text{SO}_2$ (dimethyl sulfone)	-89.2	-69.1	20.1	-69.6	19.6
$\text{C}_6\text{H}_5\text{Cl}$ (chlorobenzene)	12.4	-3.1	-15.5	-3.5	-15.9
$\text{NC}-\text{CH}_2\text{CH}_2-\text{CN}$ (succinonitrile)	50.1	48.8	-1.3	48.3	-1.8
$\text{C}_4\text{H}_4\text{N}_2$ (pyrazine)	46.9	36.6	-10.3	36.2	-10.7
$\text{CH}_3\text{COC}\equiv\text{CH}$ (acetyl acetylene)	15.6	16.5	0.9	16.1	0.5
$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$ (crotonaldehyde)	-24.0	-27.8	-3.8	-28.3	-4.3
$(\text{CH}_3\text{CO})_2\text{O}$ (acetic anhydride)	-136.8	-138.4	-1.6	-139.0	-2.2
$\text{C}_4\text{H}_6\text{S}$ (2,5-dihydrothiophene)	20.8	15.1	-5.7	14.7	-6.1
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CN}$ (2-methyl propanenitrile)	5.6	7.1	1.5	6.7	1.1
$\text{CH}_3-\text{CO}-\text{CH}_2\text{CH}_3$ (methyl ethyl ketone)	-57.1	-58.0	-0.9	-58.4	-1.3
$(\text{CH}_3)_2\text{CH}-\text{CHO}$ (isobutyraldehyde)	-51.6	-50.2	1.4	-50.7	0.9
$\text{C}_4\text{H}_8\text{O}_2$ (1,4-dioxane)	-75.5	-75.5	0.0	-76.1	-0.6
$\text{C}_4\text{H}_8\text{S}$ (tetrahydrothiophene)	-8.2	-10.9	-2.7	-11.3	-3.1
$(\text{CH}_3)_3\text{C}-\text{Cl}$ (<i>t</i> -butyl chloride)	-43.5	-43.7	-0.2	-44.0	-0.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (<i>n</i> -butyl chloride)	-37.0	-38.5	-1.5	-38.9	-1.9
$\text{C}_4\text{H}_8\text{NH}$ (pyrrolidine)	-0.8	-4.7	-3.9	-5.1	-4.3
$\text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_3$ (2-nitrobutane)	-39.1	-40.6	-1.5	-41.3	-2.2
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (diethyl ether)	-60.3	-58.1	2.2	-58.5	1.8
$\text{CH}_3-\text{CH}(\text{OCH}_3)_2$ (1,1-dimethoxy ethane)	-93.1	-87.8	5.3	-88.4	4.7
$(\text{CH}_3)_3\text{C}-\text{SH}$ (<i>t</i> -butanethiolo)	-26.2	-23.2	3.0	-23.6	2.6
$(\text{CH}_3\text{CH}_2\text{S})_2$ (diethyl disulfide)	-17.9	-15.5	2.4	-16.1	1.8

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Table A.2 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
(CH ₃) ₃ C-NH ₂ (<i>t</i> -butylamine)	-28.9	-25.9	3.0	-26.3	2.6
Si(CH ₃) ₄ (tetramethyl silane)	-55.7	-43.2	12.5	-43.6	12.1
C ₅ H ₆ S (2-methyl thiophene)	20.0	11.9	-8.1	11.5	-8.5
C ₅ H ₇ N (<i>N</i> -methyl pyrrole)	24.6	15.0	-9.6	14.6	-10.0
C ₅ H ₁₀ O (tetrahydropyran)	-53.4	-55.2	-1.8	-55.7	-2.3
C ₂ H ₅ COC ₂ H ₅ (diethyl ketone)	-61.6	-63.7	-2.1	-64.2	-2.6
CH ₃ COOCH(CH ₃) ₂ (isopropyl acetate)	-115.1	-114.2	0.9	-114.8	0.3
C ₅ H ₁₀ S (tetrahydrothiopyran)	-15.2	-18.1	-2.9	-18.6	-3.4
C ₅ H ₁₀ NH (piperidine)	-11.3	-14.5	-3.2	-15.0	-3.7
(CH ₃) ₃ COCH ₃ (<i>t</i> -butyl methyl ether)	-67.8	-63.5	4.3	-64.0	3.8
C ₆ H ₄ F ₂ (1,3-difluorobenzene)	-73.9	-89.4	-15.5	-89.9	-16.0
C ₆ H ₄ F ₂ (1,4-difluorobenzene)	-73.3	-88.7	-15.4	-89.2	-15.9
C ₆ H ₅ F (fluorobenzene)	-27.7	-41.6	-13.9	-42.0	-14.3
(CH ₃) ₂ CHOCH(CH ₃) ₂ (diisopropyl ether)	-76.3	-73.4	2.9	-74.0	2.3
PF ₅	-381.1	-341.9	39.2	-342.4	38.7
SF ₆	-291.7	-251.4	40.3	-252.2	39.5
P ₄	14.1	17.8	3.7	17.4	3.3
SO ₃	-94.6	-69.1	25.5	-69.6	25.0
SCl ₂	-4.2	-3.2	1.0	-3.5	0.7
POCl ₃	-133.8	-121.6	12.2	-122.0	11.8
PCl ₅	-86.1	-82.7	3.4	-83.3	2.8
SO ₂ Cl ₂	-84.8	-66.1	18.7	-66.6	18.2
PCl ₃	-69.0	-66.1	2.9	-66.5	2.5
S ₂ Cl ₂	-4.0	-6.6	-2.6	-7.1	-3.1
SiCl ₂ (¹ A ₁)	-40.3	-37.2	3.1	-37.4	2.9
CF ₃ Cl	-169.5	-168.8	0.7	-169.3	0.2
C ₂ F ₆	-321.3	-318.6	2.7	-319.4	1.9
CF ₃	-111.3	-113.3	-2.0	-113.6	-2.3
C ₆ H ₅ (phenyl radical)	81.2	63.1	-18.1	63.3	-17.9

Table A.3: Standard enthalpies of formation (in kcal/mol) for the G3 molecules computed using 6-311++G(3df,3pd) basis set. All values are in kcal/mol

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
<i>G3-1 subset</i>					
LiH	33.3	38.6	5.3	38.6	5.3
BeH	81.7	75.8	-5.9	75.8	-5.9
CH	142.5	143.4	0.9	143.3	0.8
CH ₂ (³ B ₁)	93.7	90.3	-3.4	90.3	-3.4
CH ₂ (¹ A ₁)	102.8	107.2	4.4	107.1	4.3
CH ₃	35.0	34.1	-0.9	34.0	-1.0
CH ₄	-17.9	-15.4	2.5	-15.4	2.5
NH	85.2	83.4	-1.8	83.4	-1.8
NH ₂	45.1	43.6	-1.5	43.6	-1.5
NH ₃	-11.0	-8.1	2.9	-8.2	2.8

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Table A.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
OH	9.4	9.8	0.4	9.8	0.4
H ₂ O	-57.8	-52.9	4.9	-52.9	4.9
FH	-65.1	-61.7	3.4	-61.7	3.4
SiH ₂ (¹ A ₁)	65.2	69.6	4.4	69.5	4.3
SiH ₂ (³ B ₁)	86.2	84.7	-1.5	84.7	-1.5
SiH ₃	47.9	49.9	2.0	49.8	1.9
SiH ₄	8.2	15.0	6.8	14.9	6.7
PH ₂	33.1	32.5	-0.6	32.4	-0.7
PH ₃	1.3	5.2	3.9	5.0	3.7
H ₂ S	-4.9	-2.7	2.2	-2.7	2.2
HCl	-22.1	-21.2	0.9	-21.2	0.9
Li ₂	51.6	56.4	4.8	56.4	4.8
LiF	-80.1	-74.7	5.4	-74.7	5.4
HC≡CH	54.2	55.2	1.0	55.2	1.0
CH ₂ =CH ₂	12.5	12.0	-0.5	11.9	-0.6
CH ₃ CH ₃	-20.1	-20.0	0.1	-20.1	0.0
CN	104.9	107.3	2.4	107.2	2.3
HCN	31.5	32.7	1.2	32.6	1.1
CO	-26.4	-23.5	2.9	-23.6	2.8
CHO	10.0	7.2	-2.8	7.1	-2.9
CH ₂ O	-26.0	-25.7	0.3	-25.9	0.1
CH ₃ OH	-48.0	-46.3	1.7	-46.4	1.6
N ₂	0.0	3.2	3.2	3.1	3.1
N ₂ H ₄	22.8	22.7	-0.1	22.5	-0.3
NO	21.6	20.5	-1.1	20.3	-1.3
O ₂	0.0	-4.2	-4.2	-4.3	-4.3
H ₂ O ₂	-32.5	-27.6	4.9	-27.7	4.8
F ₂	0.0	4.5	4.5	4.4	4.4
CO ₂	-94.1	-98.3	-4.2	-98.6	-4.5
Na ₂	34.0	34.8	0.8	34.8	0.8
Si ₂	139.9	137.6	-2.3	137.5	-2.4
P ₂	34.3	39.4	5.1	39.3	5.0
S ₂	30.7	26.1	-4.6	26.0	-4.7
Cl ₂	0.0	-0.8	-0.8	-1.0	-1.0
NaCl	-43.6	-40.1	3.5	-40.1	3.5
SiO	-24.6	-14.7	9.9	-14.8	9.8
CS	66.9	70.1	3.2	70.0	3.1
SO	1.2	-0.2	-1.4	-0.3	-1.5
ClO	24.2	21.9	-2.3	21.7	-2.5
ClF	-13.2	-12.4	0.8	-12.6	0.6
Si ₂ H ₆	19.1	27.2	8.1	26.9	7.8
CH ₃ Cl	-19.6	-21.1	-1.5	-21.2	-1.6
CH ₃ SH	-5.5	-5.2	0.3	-5.4	0.1
HOCl	-17.8	-16.3	1.5	-16.4	1.4
SO ₂	-71.0	-64.4	6.6	-64.7	6.3
<i>G3-2 subset</i>					
BF ₃	-271.4	-269.4	2.0	-269.6	1.8
BCl ₃	-96.3	-105.4	-9.1	-105.6	-9.3
AlF ₃	-289.0	-273.3	15.7	-273.4	15.6
AlCl ₃	-139.7	-140.5	-0.8	-140.6	-0.9

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Table A.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
CF ₄	-223.0	-229.2	-6.2	-229.6	-6.6
CCl ₄	-22.9	-31.1	-8.2	-31.6	-8.7
COS	-33.1	-39.1	-6.0	-39.4	-6.3
CS ₂	28.0	21.5	-6.5	21.3	-6.7
COF ₂	-149.1	-150.8	-1.7	-151.2	-2.1
SiF ₄	-386.0	-364.4	21.6	-364.7	21.3
SiCl ₄	-158.4	-158.2	0.2	-158.5	-0.1
N ₂ O	19.6	14.0	-5.6	13.7	-5.9
NOCl	12.4	9.9	-2.5	9.4	-3.0
NF ₃	-31.6	-37.5	-5.9	-38.2	-6.6
PF ₃	-229.1	-219.2	9.9	-219.5	9.6
O ₃	34.1	40.9	6.8	40.4	6.3
F ₂ O	5.9	7.8	1.9	7.3	1.4
ClF ₃	-38.0	-41.1	-3.1	-41.7	-3.7
CF ₂ =CF ₂	-157.4	-174.1	-16.7	-174.6	-17.2
CCl ₂ =CCl ₂	-3.0	-19.1	-16.1	-19.6	-16.6
CF ₃ CN	-118.4	-127.0	-8.6	-127.6	-9.2
CH ₃ C≡CH (propyne)	44.2	41.0	-3.2	40.9	-3.3
CH ₂ =C=CH ₂ (allene)	45.5	39.0	-6.5	38.8	-6.7
C ₃ H ₄ (cyclopropene)	66.2	59.9	-6.3	59.7	-6.5
CH ₃ CH=CH ₂ (propylene)	4.8	1.8	-3.0	1.6	-3.2
C ₃ H ₆ (cyclopropane)	12.7	6.0	-6.7	5.8	-6.9
C ₃ H ₈ (propane)	-25.0	-26.5	-1.5	-26.8	-1.8
C ₄ H ₆ (1,3-butadiene)	26.3	20.4	-5.9	20.1	-6.2
C ₄ H ₆ (2-butyne)	34.8	28.5	-6.3	28.2	-6.6
C ₄ H ₆ (methylene cyclopropane)	47.9	34.9	-13.0	34.6	-13.3
C ₄ H ₆ (bicyclobutane)	51.9	40.2	-11.7	39.9	-12.0
C ₄ H ₆ (cyclobutene)	37.4	29.1	-8.3	28.8	-8.6
C ₄ H ₈ (cyclobutane)	6.8	-1.4	-8.2	-1.7	-8.5
C ₄ H ₈ (isobutene)	-4.0	-8.4	-4.4	-8.7	-4.7
C ₄ H ₁₀ (butane)	-30.0	-33.0	-3.0	-33.4	-3.4
C ₄ H ₁₀ (isobutane)	-32.1	-34.2	-2.1	-34.5	-2.4
C ₅ H ₈ (spiropentane)	44.3	28.0	-16.3	27.6	-16.7
C ₆ H ₆ (benzene)	19.7	1.2	-18.5	0.9	-18.8
CH ₂ F ₂	-107.7	-109.8	-2.1	-110.0	-2.3
CHF ₃	-166.6	-170.5	-3.9	-170.9	-4.3
CH ₂ Cl ₂	-22.8	-27.2	-4.4	-27.4	-4.6
CHCl ₃	-24.7	-31.2	-6.5	-31.5	-6.8
CH ₃ NH ₂ (methylamine)	-5.5	-5.1	0.4	-5.3	0.2
CH ₃ CN (acetonitrile)	18.0	15.1	-2.9	14.9	-3.1
CH ₃ NO ₂ (nitromethane)	-17.8	-24.5	-6.7	-25.0	-7.2
CH ₃ ONO (methyl nitrite)	-15.9	-19.3	-3.4	-19.9	-4.0
CH ₃ SiH ₃ (methyl silane)	-7.0	-0.7	6.3	-0.9	6.1
HCOOH (formic acid)	-90.5	-92.0	-1.5	-92.3	-1.8
HCOOCH ₃ (methyl formate)	-85.0	-89.0	-4.0	-89.4	-4.4
CH ₃ CONH ₂ (acetamide)	-57.0	-62.4	-5.4	-62.7	-5.7
C ₂ H ₄ NH (aziridine)	30.2	23.6	-6.6	23.3	-6.9
(CN) ₂ (cyanogen)	73.3	69.3	-4.0	68.9	-4.4
(CH ₃) ₂ NH (dimethylamine)	-4.4	-6.0	-1.6	-6.3	-1.9
CH ₃ CH ₂ NH ₂ (ethylamine)	-11.3	-13.5	-2.2	-13.8	-2.5

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Table A.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
CH ₂ =C=O (ketene)	-11.4	-18.2	-6.8	-18.4	-7.0
C ₂ H ₄ O (oxirane)	-12.6	-17.6	-5.0	-17.8	-5.2
CH ₃ CHO (acetaldehyde)	-39.7	-42.2	-2.5	-42.4	-2.7
HCOCHO (glyoxal)	-50.7	-54.8	-4.1	-55.2	-4.5
CH ₃ CH ₂ OH (ethanol)	-56.2	-56.1	0.1	-56.3	-0.1
CH ₃ OCH ₃ (dimethyl ether)	-44.0	-44.3	-0.3	-44.6	-0.6
C ₂ H ₄ S (thiirane)	19.6	13.0	-6.6	12.8	-6.8
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-35.9	0.3	-36.3	-0.1
C ₂ H ₅ SH (ethanethiol)	-11.1	-12.1	-1.0	-12.4	-1.3
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	-10.4	-1.5	-10.7	-1.8
CH ₂ =CHF (vinyl fluoride)	-33.2	-37.8	-4.6	-38.0	-4.8
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-30.0	-3.2	-30.2	-3.4
CH ₂ =CHCl (vinyl chloride)	8.9	0.6	-8.3	0.3	-8.6
CH ₂ =CHCN (acrylonitrile)	43.2	39.3	-3.9	39.0	-4.2
CH ₃ COCH ₃ (acetone)	-51.9	-56.2	-4.3	-56.6	-4.7
CH ₃ COOH (acetic acid)	-103.4	-106.7	-3.3	-107.1	-3.7
CH ₃ COF (acetyl fluoride)	-105.7	-110.3	-4.6	-110.7	-5.0
CH ₃ COCl (acetyl chloride)	-58.0	-64.4	-6.4	-64.8	-6.8
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-36.5	-5.0	-36.8	-5.3
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-66.2	-1.0	-66.6	-1.4
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-54.0	-2.3	-54.4	-2.7
(CH ₃) ₃ N (trimethylamine)	-5.7	-9.0	-3.3	-9.3	-3.6
C ₄ H ₄ O (furan)	-8.3	-21.7	-13.4	-22.0	-13.7
C ₄ H ₄ S (thiophene)	27.5	14.1	-13.4	13.7	-13.8
C ₄ H ₅ N (pyrrole)	25.9	9.8	-16.1	9.5	-16.4
C ₅ H ₅ N (pyridine)	33.6	14.2	-19.4	13.8	-19.8
H ₂	0.0	5.3	5.3	5.3	5.3
SH	34.2	34.1	-0.1	34.1	-0.1
C≡CH (² A', C _s)	135.1	134.2	-0.9	134.2	-0.9
CH=CH ₂ (² A', C _s)	71.6	66.5	-5.1	66.4	-5.2
CH ₃ CO (² A', C _s)	-2.4	-8.3	-5.9	-8.6	-6.2
CH ₂ OH (² A, C ₁)	-4.1	-6.4	-2.3	-6.6	-2.5
CH ₃ O (² A', C _s)	4.1	0.6	-3.5	0.4	-3.7
CH ₃ CH ₂ O (² A'', C _s)	-3.7	-10.1	-6.4	-10.5	-6.8
CH ₃ S (² A', C _s)	29.8	26.3	-3.5	26.1	-3.7
CH ₃ CH ₂ (² A', C _s)	28.9	24.9	-4.0	24.7	-4.2
(CH ₃) ₂ CH (² A', C _s)	21.5	14.8	-6.7	14.5	-7.0
(CH ₃) ₃ C (<i>t</i> -butyl radical, C _{3v})	12.3	4.5	-7.8	4.2	-8.1
NO ₂	7.9	0.6	-7.3	0.3	-7.6
<i>G3-3 subset</i>					
CH ₂ =C=CHCH ₃ (1,2-butadiene)	38.8	30.5	-8.3	30.2	-8.6
CH ₂ =CH-C(CH ₃)=CH ₂ (isoprene)	18.0	11.0	-7.0	10.5	-7.5
C ₅ H ₁₂ (<i>n</i> -pentane)	-35.1	-39.4	-4.3	-39.9	-4.8
C(CH ₃) ₄ (neopentane)	-40.2	-42.0	-1.8	-42.5	-2.3
C ₆ H ₈ (1,3-cyclohexadiene)	25.4	12.0	-13.4	11.5	-13.9
C ₆ H ₈ (1,4-cyclohexadiene)	25.0	11.8	-13.2	11.3	-13.7
C ₆ H ₁₂ (cyclohexane)	-29.5	-38.5	-9.0	-39.0	-9.5
C ₆ H ₁₄ (<i>n</i> -hexane)	-39.9	-45.8	-5.9	-46.4	-6.5
C ₆ H ₁₄ (3-methyl pentane)	-41.1	-45.2	-4.1	-45.8	-4.7
C ₆ H ₅ CH ₃ (toluene)	12.0	-7.9	-19.9	-8.4	-20.4

Continued on next page

Table A.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
C ₇ H ₁₆ (<i>n</i> -heptane)	-44.9	-52.3	-7.4	-52.9	-8.0
C ₈ H ₈ (1,3,5,7-cyclooctatetraene)	70.7	52.0	-18.7	51.2	-19.5
C ₈ H ₁₈ (<i>n</i> -octane)	-49.9	-58.7	-8.8	-59.4	-9.5
C ₁₀ H ₈ (naphthalene)	35.9	0.9	-35.0	0.3	-35.6
C ₁₀ H ₈ (azulene)	69.1	35.1	-34.0	34.5	-34.6
CH ₃ COOCH ₃ (methyl acetate)	-98.4	-103.2	-4.8	-103.7	-5.3
(CH ₃) ₃ COH (<i>t</i> -butanol)	-74.7	-75.7	-1.0	-76.2	-1.5
C ₆ H ₅ NH ₂ (aniline)	20.8	-1.0	-21.8	-1.5	-22.3
C ₆ H ₅ OH (phenol)	-23.0	-42.1	-19.1	-42.6	-19.6
CH ₂ =CH-O-CH=CH ₂ (divinyl ether)	-3.3	-10.9	-7.6	-11.4	-8.1
C ₄ H ₈ O (tetrahydrofuran)	-44.0	-51.3	-7.3	-51.8	-7.8
C ₅ H ₈ O (cyclopentanone)	-45.9	-58.7	-12.8	-59.3	-13.4
C ₆ H ₄ O ₂ (1,4-benzoquinone)	-29.4	-47.0	-17.6	-47.9	-18.5
C ₄ H ₄ N ₂ (pyrimidine)	46.8	25.2	-21.6	24.8	-22.0
(CH ₃) ₂ SO ₂ (dimethyl sulfone)	-89.2	-86.6	2.6	-87.1	2.1
C ₆ H ₅ Cl (chlorobenzene)	12.4	-9.7	-22.1	-10.1	-22.5
NC-CH ₂ CH ₂ -CN (succinonitrile)	50.1	42.0	-8.1	41.5	-8.6
C ₄ H ₄ N ₂ (pyrazine)	46.9	29.5	-17.4	29.0	-17.9
CH ₃ COC≡CH (acetyl acetylene)	15.6	11.2	-4.4	10.7	-4.9
CH ₃ -CH=CH-CHO (crotonaldehyde)	-24.0	-33.0	-9.0	-33.5	-9.5
(CH ₃ CO) ₂ O (acetic anhydride)	-136.8	-147.3	-10.5	-148.0	-11.2
C ₄ H ₆ S (2,5-dihydrothiophene)	20.8	10.0	-10.8	9.6	-11.2
CH ₃ CH(CH ₃)CN (2-methyl propanenitrile)	5.6	2.0	-3.6	1.6	-4.0
CH ₃ -CO-CH ₂ CH ₃ (methyl ethyl ketone)	-57.1	-62.9	-5.8	-63.4	-6.3
(CH ₃) ₂ CH-CHO (isobutyraldehyde)	-51.6	-55.4	-3.8	-55.8	-4.2
C ₄ H ₈ O ₂ (1,4-dioxane)	-75.5	-83.0	-7.5	-83.7	-8.2
C ₄ H ₈ S (tetrahydrothiophene)	-8.2	-15.9	-7.7	-16.4	-8.2
(CH ₃) ₃ C-Cl (<i>t</i> -butyl chloride)	-43.5	-48.1	-4.6	-48.5	-5.0
CH ₃ CH ₂ CH ₂ CH ₂ Cl (<i>n</i> -butyl chloride)	-37.0	-42.8	-5.8	-43.3	-6.3
C ₄ H ₈ NH (pyrrolidine)	-0.8	-10.0	-9.2	-10.4	-9.6
CH ₃ CH ₂ CH(NO ₂)CH ₃ (2-nitrobutane)	-39.1	-48.5	-9.4	-49.2	-10.1
CH ₃ CH ₂ OCH ₂ CH ₃ (diethyl ether)	-60.3	-63.7	-3.4	-64.1	-3.8
CH ₃ -CH(OCH ₃) ₂ (1,1-dimethoxy ethane)	-93.1	-95.6	-2.5	-96.2	-3.1
(CH ₃) ₃ C-SH (<i>t</i> -butanethiol)	-26.2	-28.2	-2.0	-28.7	-2.5
(CH ₃ CH ₂ S) ₂ (diethyl disulfide)	-17.9	-22.5	-4.6	-23.1	-5.2
(CH ₃) ₃ C-NH ₂ (<i>t</i> -butylamine)	-28.9	-31.1	-2.2	-31.6	-2.7
Si(CH ₃) ₄ (tetramethyl silane)	-55.7	-49.3	6.4	-49.7	6.0
C ₅ H ₆ S (2-methyl thiophene)	20.0	4.9	-15.1	4.4	-15.6
C ₅ H ₇ N (<i>N</i> -methyl pyrrole)	24.6	7.4	-17.2	7.0	-17.6
C ₅ H ₁₀ O (tetrahydropyran)	-53.4	-61.5	-8.1	-62.1	-8.7
C ₂ H ₅ COC ₂ H ₅ (diethyl ketone)	-61.6	-69.4	-7.8	-70.0	-8.4
CH ₃ COOCH(CH ₃) ₂ (isopropyl acetate)	-115.1	-122.2	-7.1	-122.9	-7.8
C ₅ H ₁₀ S (tetrahydrothiopyran)	-15.2	-24.1	-8.9	-24.7	-9.5
C ₅ H ₁₀ NH (piperidine)	-11.3	-20.6	-9.3	-21.2	-9.9
(CH ₃) ₃ COCH ₃ (<i>t</i> -butyl methyl ether)	-67.8	-70.0	-2.2	-70.6	-2.8
C ₆ H ₄ F ₂ (1,3-difluorobenzene)	-73.9	-98.7	-24.8	-99.3	-25.4
C ₆ H ₄ F ₂ (1,4-difluorobenzene)	-73.3	-97.9	-24.6	-98.4	-25.1
C ₆ H ₅ F (fluorobenzene)	-27.7	-49.0	-21.3	-49.5	-21.8
(CH ₃) ₂ CHOCH(CH ₃) ₂ (diisopropyl ether)	-76.3	-80.6	-4.3	-81.3	-5.0
PF ₅	-381.1	-366.1	15.0	-366.6	14.5

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Table A.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
SF ₆	-291.7	-285.6	6.1	-286.3	5.4
P ₄	14.1	10.0	-4.1	9.6	-4.5
SO ₃	-94.6	-89.0	5.6	-89.5	5.1
SCl ₂	-4.2	-6.9	-2.7	-7.3	-3.1
POCl ₃	-133.8	-133.0	0.8	-133.4	0.4
PCl ₅	-86.1	-93.3	-7.2	-93.8	-7.7
SO ₂ Cl ₂	-84.8	-83.2	1.6	-83.7	1.1
PCl ₃	-69.0	-71.6	-2.6	-72.0	-3.0
S ₂ Cl ₂	-4.0	-11.7	-7.7	-12.3	-8.3
SiCl ₂ (¹ A ₁)	-40.3	-40.0	0.3	-40.2	0.1
CF ₃ Cl	-169.5	-177.5	-8.0	-177.9	-8.4
C ₂ F ₆	-321.3	-333.1	-11.8	-333.8	-12.5
CF ₃	-111.3	-121.0	-9.7	-121.3	-10.0
C ₅ H ₁₀ (cyclopentane)	-18.3	-27.2	-8.9	-27.6	-9.3
C ₆ H ₅ (phenyl radical)	81.2	58.0	-23.2	57.6	-23.6

Appendix B

Standard enthalpies of formation of G3-2 test set using Dunning’s correlation-consistent basis sets

Table B.1: Standard enthalpies of formation (in kcal/mol) for the G3-2 molecules computed using cc-pVDZ basis set. All values are in kcal/mol

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
BF ₃	-271.4	-257.7	13.7	-257.8	13.6
BCl ₃	-96.3	-98.3	-2.0	-98.5	-2.2
AlF ₃	-289.0	-246.7	42.3	-246.8	42.2
AlCl ₃	-139.7	-124.9	14.8	-125.0	14.7
CF ₄	-223.0	-222.8	0.2	-223.2	-0.2
CCl ₄	-22.9	-19.4	3.5	-19.9	3.0
COS	-33.1	-31.2	1.9	-31.4	1.7
CS ₂	28.0	30.6	2.6	30.4	2.4
COF ₂	-149.1	-143.6	5.5	-144.0	5.1
SiF ₄	-386.0	-319.0	67.0	-319.2	66.8
SiCl ₄	-158.4	-137.7	20.7	-138.0	20.4
N ₂ O	19.6	20.6	1.0	20.3	0.7
NOCl	12.4	13.8	1.4	13.5	1.1
NF ₃	-31.6	-29.6	2.0	-30.2	1.4
PF ₃	-229.1	-187.0	42.1	-187.3	41.8
O ₃	34.1	46.5	12.4	46.1	12.0
F ₂ O	5.9	11.0	5.1	10.5	4.6
ClF ₃	-38.0	-13.9	24.1	-14.4	23.6
CF ₂ =CF ₂	-157.4	-162.8	-5.4	-163.3	-5.9
CCl ₂ =CCl ₂	-3.0	-3.5	-0.5	-4.0	-1.0
CF ₃ CN	-118.4	-116.2	2.2	-116.7	1.7
CH ₃ C≡CH (propyne)	44.2	52.4	8.2	52.3	8.1
CH ₂ =C=CH ₂ (allene)	45.5	49.7	4.2	49.5	4.0
C ₃ H ₄ (cyclopropene)	66.2	69.9	3.7	69.8	3.6
CH ₃ CH=CH ₂ (propylene)	4.8	12.3	7.5	12.1	7.3
C ₃ H ₆ (cyclopropane)	12.7	16.5	3.8	16.3	3.6
C ₃ H ₈ (propane)	-25.0	-16.0	9.0	-16.2	8.8

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Table B.1 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
C ₄ H ₆ (1,3-butadiene)	26.3	33.2	6.9	32.9	6.6
C ₄ H ₆ (2-butyne)	34.8	42.4	7.6	42.1	7.3
C ₄ H ₆ (methylene cyclopropane)	47.9	47.6	-0.3	47.4	-0.5
C ₄ H ₆ (bicyclobutane)	51.9	52.0	0.1	51.8	-0.1
C ₄ H ₆ (cyclobutene)	37.4	40.1	2.7	39.8	2.4
C ₄ H ₈ (cyclobutane)	6.8	10.1	3.3	9.9	3.1
C ₄ H ₈ (isobutene)	-4.0	4.8	8.8	4.5	8.5
C ₄ H ₁₀ (butane)	-30.0	-19.9	10.1	-20.2	9.8
C ₄ H ₁₀ (isobutane)	-32.1	-20.9	11.2	-21.2	10.9
C ₅ H ₈ (spiropentane)	44.3	43.0	-1.3	42.7	-1.6
C ₆ H ₆ (benzene)	19.7	15.9	-3.8	15.6	-4.1
CH ₂ F ₂	-107.7	-100.5	7.2	-100.7	7.0
CHF ₃	-166.6	-162.1	4.5	-162.5	4.1
CH ₂ Cl ₂	-22.8	-18.2	4.6	-18.4	4.4
CHCl ₃	-24.7	-20.5	4.2	-20.9	3.8
CH ₃ NH ₂ (methylamine)	-5.5	6.3	11.8	6.2	11.7
CH ₃ CN (acetonitrile)	18.0	25.1	7.1	24.9	6.9
CH ₃ NO ₂ (nitromethane)	-17.8	-13.2	4.6	-13.6	4.2
CH ₃ ONO (methyl nitrite)	-15.9	-9.9	6.0	-10.4	5.5
CH ₃ SiH ₃ (methyl silane)	-7.0	10.1	17.1	9.9	16.9
HCOOH (formic acid)	-90.5	-82.2	8.3	-82.4	8.1
HCOOCH ₃ (methyl formate)	-85.0	-76.7	8.3	-77.0	8.0
CH ₃ CONH ₂ (acetamide)	-57.0	-47.0	10.0	-47.3	9.7
C ₂ H ₄ NH (aziridine)	30.2	35.8	5.6	35.6	5.4
(CN) ₂ (cyanogen)	73.3	80.2	6.9	79.8	6.5
(CH ₃) ₂ NH (dimethylamine)	-4.4	6.8	11.2	6.6	11.0
CH ₃ CH ₂ NH ₂ (ethylamine)	-11.3	-0.1	11.2	-0.3	11.0
CH ₂ =C=O (ketene)	-11.4	-9.2	2.2	-9.4	2.0
C ₂ H ₄ O (oxirane)	-12.6	-6.5	6.1	-6.7	5.9
CH ₃ CHO (acetaldehyde)	-39.7	-32.5	7.2	-32.7	7.0
HCOCHO (glyoxal)	-50.7	-44.5	6.2	-44.8	5.9
CH ₃ CH ₂ OH (ethanol)	-56.2	-42.9	13.3	-43.1	13.1
CH ₃ OCH ₃ (dimethyl ether)	-44.0	-32.7	11.3	-33.0	11.0
C ₂ H ₄ S (thiirane)	19.6	23.6	4.0	23.5	3.9
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-2.1	34.1	-2.5	33.7
C ₂ H ₅ SH (ethanethiol)	-11.1	-0.9	10.2	-1.1	10.0
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	2.0	10.9	1.8	10.7
CH ₂ =CHF (vinyl fluoride)	-33.2	-28.4	4.8	-28.6	4.6
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-20.3	6.5	-20.5	6.3
CH ₂ =CHCl (vinyl chloride)	8.9	10.0	1.1	9.8	0.9
CH ₂ =CHCN (acrylonitrile)	43.2	51.6	8.4	51.3	8.1
CH ₃ COCH ₃ (acetone)	-51.9	-43.8	8.1	-44.1	7.8
CH ₃ COOH (acetic acid)	-103.4	-94.1	9.3	-94.4	9.0
CH ₃ COF (acetyl fluoride)	-105.7	-99.9	5.8	-100.2	5.5
CH ₃ COCl (acetyl chloride)	-58.0	-54.0	4.0	-54.4	3.6
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-24.0	7.5	-24.3	7.2
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-50.8	14.4	-51.1	14.1
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-39.9	11.8	-40.3	11.4
(CH ₃) ₃ N (trimethylamine)	-5.7	5.7	11.4	5.3	11.0
C ₄ H ₄ O (furan)	-8.3	-9.1	-0.8	-9.4	-1.1

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Table B.1 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
C ₄ H ₄ S (thiophene)	27.5	29.8	2.3	29.5	2.0
C ₄ H ₅ N (pyrrole)	25.9	24.5	-1.4	24.2	-1.7
C ₅ H ₅ N (pyridine)	33.6	29.4	-4.2	29.1	-4.5
H ₂	0.0	7.4	7.4	7.4	7.4
SH	34.2	36.8	2.6	36.8	2.6
C≡CH (² A', C _s)	135.1	141.1	6.0	141.0	5.9
CH=CH ₂ (² A', C _s)	71.6	73.9	2.3	73.8	2.2
CH ₃ CO (² A', C _s)	-2.4	0.7	3.1	0.5	2.9
CH ₂ OH (² A, C ₁)	-4.1	3.1	7.2	3.0	7.1
CH ₃ O (² A', C _s)	4.1	7.9	3.8	7.7	3.6
CH ₃ CH ₂ O (² A'', C _s)	-3.7	-0.4	3.3	-0.7	3.0
CH ₃ S (² A', C _s)	29.8	32.9	3.1	32.8	3.0
CH ₃ CH ₂ (² A', C _s)	28.9	32.6	3.7	32.5	3.6
(CH ₃) ₂ CH (² A', C _s)	21.5	25.0	3.5	24.8	3.3
(CH ₃) ₃ C (<i>t</i> -butyl radical, C _{3v})	12.3	17.3	5.0	17.0	4.7
NO ₂	7.9	5.9	-2.0	5.6	-2.3

Table B.2: Standard enthalpies of formation (in kcal/mol) for the G3-2 molecules computed using cc-pVTZ basis set. All values are in kcal/mol

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
BF ₃	-271.4	-269.2	2.2	-269.4	2.0
BCl ₃	-96.3	-100.8	-4.5	-101.0	-4.7
AlF ₃	-289.0	-268.2	20.8	-268.3	20.7
AlCl ₃	-139.7	-135.4	4.3	-135.5	4.2
CF ₄	-223.0	-227.7	-4.7	-228.1	-5.1
CCl ₄	-22.9	-24.9	-2.0	-25.4	-2.5
COS	-33.1	-36.3	-3.2	-36.5	-3.4
CS ₂	28.0	25.2	-2.8	25.0	-3.0
COF ₂	-149.1	-149.1	0.0	-149.5	-0.4
SiF ₄	-386.0	-359.4	26.6	-359.6	26.4
SiCl ₄	-158.4	-151.7	6.7	-152.0	6.4
N ₂ O	19.6	15.0	-4.6	14.7	-4.9
NOCl	12.4	11.2	-1.2	10.8	-1.6
NF ₃	-31.6	-36.1	-4.5	-36.8	-5.2
PF ₃	-229.1	-214.4	14.7	-214.7	14.4
O ₃	34.1	42.0	7.9	41.6	7.5
F ₂ O	5.9	6.7	0.8	6.2	0.3
ClF ₃	-38.0	-34.6	3.4	-35.1	2.9
CF ₂ =CF ₂	-157.4	-171.2	-13.8	-171.7	-14.3
CCl ₂ =CCl ₂	-3.0	-12.2	-9.2	-12.7	-9.7
CF ₃ CN	-118.4	-124.5	-6.1	-125.0	-6.6
CH ₃ C≡CH (propyne)	44.2	41.7	-2.5	41.5	-2.7
CH ₂ =C=CH ₂ (allene)	45.5	39.8	-5.7	39.6	-5.9
C ₃ H ₄ (cyclopropene)	66.2	60.8	-5.4	60.6	-5.6
CH ₃ CH=CH ₂ (propylene)	4.8	2.4	-2.4	2.2	-2.6

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Table B.2 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
C ₃ H ₆ (cyclopropane)	12.7	6.7	-6.0	6.5	-6.2
C ₃ H ₈ (propane)	-25.0	-26.2	-1.2	-26.5	-1.5
C ₄ H ₆ (1,3-butadiene)	26.3	21.3	-5.0	21.0	-5.3
C ₄ H ₆ (2-butyne)	34.8	29.3	-5.5	29.0	-5.8
C ₄ H ₆ (methylene cyclopropane)	47.9	35.9	-12.0	35.7	-12.2
C ₄ H ₆ (bicyclobutane)	51.9	41.5	-10.4	41.3	-10.6
C ₄ H ₆ (cyclobutene)	37.4	30.0	-7.4	29.7	-7.7
C ₄ H ₈ (cyclobutane)	6.8	-0.6	-7.4	-0.9	-7.7
C ₄ H ₈ (isobutene)	-4.0	-7.7	-3.7	-8.0	-4.0
C ₄ H ₁₀ (butane)	-30.0	-32.5	-2.5	-32.8	-2.8
C ₄ H ₁₀ (isobutane)	-32.1	-33.6	-1.5	-33.9	-1.8
C ₅ H ₈ (spiropentane)	44.3	29.4	-14.9	29.0	-15.3
C ₆ H ₆ (benzene)	19.7	2.4	-17.3	2.1	-17.6
CH ₂ F ₂	-107.7	-107.7	0.0	-107.9	-0.2
CHF ₃	-166.6	-168.6	-2.0	-168.9	-2.3
CH ₂ Cl ₂	-22.8	-24.2	-1.4	-24.4	-1.6
CHCl ₃	-24.7	-26.6	-1.9	-27.0	-2.3
CH ₃ NH ₂ (methylamine)	-5.5	-3.3	2.2	-3.5	2.0
CH ₃ CN (acetonitrile)	18.0	16.4	-1.6	16.2	-1.8
CH ₃ NO ₂ (nitromethane)	-17.8	-21.7	-3.9	-22.2	-4.4
CH ₃ ONO (methyl nitrite)	-15.9	-17.1	-1.2	-17.6	-1.7
CH ₃ SiH ₃ (methyl silane)	-7.0	0.9	7.9	0.7	7.7
HCOOH (formic acid)	-90.5	-89.4	1.1	-89.6	0.9
HCOOCH ₃ (methyl formate)	-85.0	-86.2	-1.2	-86.6	-1.6
CH ₃ CONH ₂ (acetamide)	-57.0	-59.3	-2.3	-59.7	-2.7
C ₂ H ₄ NH (aziridine)	30.2	25.5	-4.7	25.3	-4.9
(CN) ₂ (cyanogen)	73.3	71.3	-2.0	71.0	-2.3
(CH ₃) ₂ NH (dimethylamine)	-4.4	-4.3	0.1	-4.5	-0.1
CH ₃ CH ₂ NH ₂ (ethylamine)	-11.3	-11.8	-0.5	-12.0	-0.7
CH ₂ =C=O (ketene)	-11.4	-16.6	-5.2	-16.8	-5.4
C ₂ H ₄ O (oxirane)	-12.6	-15.6	-3.0	-15.8	-3.2
CH ₃ CHO (acetaldehyde)	-39.7	-40.4	-0.7	-40.6	-0.9
HCOCHO (glyoxal)	-50.7	-51.7	-1.0	-52.1	-1.4
CH ₃ CH ₂ OH (ethanol)	-56.2	-53.9	2.3	-54.1	2.1
CH ₃ OCH ₃ (dimethyl ether)	-44.0	-42.5	1.5	-42.8	1.2
C ₂ H ₄ S (thiirane)	19.6	14.8	-4.8	14.6	-5.0
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-28.3	7.9	-28.7	7.5
C ₂ H ₅ SH (ethanethiol)	-11.1	-10.3	0.8	-10.5	0.6
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	-8.7	0.2	-9.0	-0.1
CH ₂ =CHF (vinyl fluoride)	-33.2	-36.4	-3.2	-36.6	-3.4
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-28.2	-1.4	-28.4	-1.6
CH ₂ =CHCl (vinyl chloride)	8.9	2.4	-6.5	2.2	-6.7
CH ₂ =CHCN (acrylonitrile)	43.2	40.8	-2.4	40.5	-2.7
CH ₃ COCH ₃ (acetone)	-51.9	-54.2	-2.3	-54.6	-2.7
CH ₃ COOH (acetic acid)	-103.4	-103.9	-0.5	-104.2	-0.8
CH ₃ COF (acetyl fluoride)	-105.7	-108.1	-2.4	-108.5	-2.8
CH ₃ COCl (acetyl chloride)	-58.0	-61.5	-3.5	-61.9	-3.9
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-34.4	-2.9	-34.7	-3.2
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-63.9	1.3	-64.2	1.0
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-52.2	-0.5	-52.6	-0.9

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Table B.2 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
(CH ₃) ₃ N (trimethylamine)	-5.7	-7.2	-1.5	-7.5	-1.8
C ₄ H ₄ O (furan)	-8.3	-19.7	-11.4	-20.1	-11.8
C ₄ H ₄ S (thiophene)	27.5	17.0	-10.5	16.7	-10.8
C ₄ H ₅ N (pyrrole)	25.9	12.0	-13.9	11.7	-14.2
C ₅ H ₅ N (pyridine)	33.6	16.5	-17.1	16.1	-17.5
H ₂	0.0	5.2	5.2	5.2	5.2
SH	34.2	35.1	0.9	35.0	0.8
C≡CH (² A', C _s)	135.1	134.7	-0.4	134.6	-0.5
CH=CH ₂ (² A', C _s)	71.6	67.1	-4.5	67.0	-4.6
CH ₃ CO (² A', C _s)	-2.4	-6.4	-4.0	-6.7	-4.3
CH ₂ OH (² A, C ₁)	-4.1	-4.4	-0.3	-4.5	-0.4
CH ₃ O (² A', C _s)	4.1	2.1	-2.0	1.8	-2.3
CH ₃ CH ₂ O (² A'', C _s)	-3.7	-8.6	-4.9	-8.9	-5.2
CH ₃ S (² A', C _s)	29.8	27.3	-2.5	27.1	-2.7
CH ₃ CH ₂ (² A', C _s)	28.9	25.2	-3.7	25.1	-3.8
(CH ₃) ₂ CH (² A', C _s)	21.5	15.3	-6.2	15.0	-6.5
(CH ₃) ₃ C (<i>t</i> -butyl radical, C _{3v})	12.3	5.2	-7.1	4.8	-7.5
NO ₂	7.9	2.2	-5.7	1.9	-6.0

Table B.3: Standard enthalpies of formation (in kcal/mol) for the G3-2 molecules computed using cc-pVQZ basis set. All values are in kcal/mol

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
BF ₃	-271.4	-268.9	2.5	-269.1	2.3
BCl ₃	-96.3	-101.6	-5.3	-101.8	-5.5
AlF ₃	-289.0	-275.1	13.9	-275.2	13.8
AlCl ₃	-139.7	-137.5	2.2	-137.6	2.1
CF ₄	-223.0	-226.8	-3.8	-227.3	-4.3
CCl ₄	-22.9	-26.8	-3.9	-27.3	-4.4
COS	-33.1	-37.6	-4.5	-37.8	-4.7
CS ₂	28.0	23.5	-4.5	23.3	-4.7
COF ₂	-149.1	-149.2	-0.1	-149.6	-0.5
SiF ₄	-386.0	-367.2	18.8	-367.4	18.6
SiCl ₄	-158.4	-154.6	3.8	-154.8	3.6
N ₂ O	19.6	14.1	-5.5	13.8	-5.8
NOCl	12.4	10.5	-1.9	10.1	-2.3
NF ₃	-31.6	-36.6	-5.0	-37.3	-5.7
PF ₃	-229.1	-219.2	9.9	-219.5	9.6
O ₃	34.1	41.1	7.0	40.6	6.5
F ₂ O	5.9	6.8	0.9	6.3	0.4
ClF ₃	-38.0	-39.1	-1.1	-39.7	-1.7
CF ₂ =CF ₂	-157.4	-171.2	-13.8	-171.8	-14.4
CCl ₂ =CCl ₂	-3.0	-14.6	-11.6	-15.1	-12.1
CF ₃ CN	-118.4	-124.5	-6.1	-125.1	-6.7
CH ₃ C≡CH (propyne)	44.2	40.8	-3.4	40.6	-3.6
CH ₂ =C=CH ₂ (allene)	45.5	39.0	-6.5	38.7	-6.8

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Table B.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
C ₃ H ₄ (cyclopropene)	66.2	59.8	-6.4	59.6	-6.6
CH ₃ CH=CH ₂ (propylene)	4.8	1.6	-3.2	1.4	-3.4
C ₃ H ₆ (cyclopropane)	12.7	5.8	-6.9	5.6	-7.1
C ₃ H ₈ (propane)	-25.0	-26.9	-1.9	-27.2	-2.2
C ₄ H ₆ (1,3-butadiene)	26.3	20.3	-6.0	19.9	-6.4
C ₄ H ₆ (2-butyne)	34.8	28.2	-6.6	27.9	-6.9
C ₄ H ₆ (methylene cyclopropane)	47.9	34.8	-13.1	34.5	-13.4
C ₄ H ₆ (bicyclobutane)	51.9	40.2	-11.7	40.0	-11.9
C ₄ H ₆ (cyclobutene)	37.4	28.9	-8.5	28.5	-8.9
C ₄ H ₈ (cyclobutane)	6.8	-1.6	-8.4	-1.9	-8.7
C ₄ H ₈ (isobutene)	-4.0	-8.7	-4.7	-9.1	-5.1
C ₄ H ₁₀ (butane)	-30.0	-33.4	-3.4	-33.8	-3.8
C ₄ H ₁₀ (isobutane)	-32.1	-34.5	-2.4	-34.9	-2.8
C ₅ H ₈ (spiropentane)	44.3	27.9	-16.4	27.6	-16.7
C ₆ H ₆ (benzene)	19.7	0.8	-18.9	0.5	-19.2
CH ₂ F ₂	-107.7	-108.2	-0.5	-108.5	-0.8
CHF ₃	-166.6	-168.5	-1.9	-168.9	-2.3
CH ₂ Cl ₂	-22.8	-25.2	-2.4	-25.4	-2.6
CHCl ₃	-24.7	-28.0	-3.3	-28.4	-3.7
CH ₃ NH ₂ (methylamine)	-5.5	-4.7	0.8	-4.8	0.7
CH ₃ CN (acetonitrile)	18.0	15.3	-2.7	15.1	-2.9
CH ₃ NO ₂ (nitromethane)	-17.8	-23.4	-5.6	-23.9	-6.1
CH ₃ ONO (methyl nitrite)	-15.9	-18.1	-2.2	-18.7	-2.8
CH ₃ SiH ₃ (methyl silane)	-7.0	-0.7	6.3	-0.9	6.1
HCOOH (formic acid)	-90.5	-90.5	0.0	-90.8	-0.3
HCOOCH ₃ (methyl formate)	-85.0	-87.4	-2.4	-87.8	-2.8
CH ₃ CONH ₂ (acetamide)	-57.0	-61.2	-4.2	-61.6	-4.6
C ₂ H ₄ NH (aziridine)	30.2	24.1	-6.1	23.8	-6.4
(CN) ₂ (cyanogen)	73.3	70.0	-3.3	69.6	-3.7
(CH ₃) ₂ NH (dimethylamine)	-4.4	-5.6	-1.2	-5.9	-1.5
CH ₃ CH ₂ NH ₂ (ethylamine)	-11.3	-13.3	-2.0	-13.5	-2.2
CH ₂ =C=O (ketene)	-11.4	-17.5	-6.1	-17.7	-6.3
C ₂ H ₄ O (oxirane)	-12.6	-16.6	-4.0	-16.9	-4.3
CH ₃ CHO (acetaldehyde)	-39.7	-41.4	-1.7	-41.7	-2.0
HCOCHO (glyoxal)	-50.7	-53.1	-2.4	-53.5	-2.8
CH ₃ CH ₂ OH (ethanol)	-56.2	-55.3	0.9	-55.5	0.7
CH ₃ OCH ₃ (dimethyl ether)	-44.0	-43.5	0.5	-43.8	0.2
C ₂ H ₄ S (thiirane)	19.6	13.6	-6.0	13.4	-6.2
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-33.1	3.1	-33.6	2.6
C ₂ H ₅ SH (ethanethiol)	-11.1	-11.4	-0.3	-11.7	-0.6
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	-9.9	-1.0	-10.2	-1.3
CH ₂ =CHF (vinyl fluoride)	-33.2	-37.0	-3.8	-37.2	-4.0
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-29.0	-2.2	-29.3	-2.5
CH ₂ =CHCl (vinyl chloride)	8.9	1.5	-7.4	1.3	-7.6
CH ₂ =CHCN (acrylonitrile)	43.2	39.5	-3.7	39.2	-4.0
CH ₃ COCH ₃ (acetone)	-51.9	-55.5	-3.6	-55.9	-4.0
CH ₃ COOH (acetic acid)	-103.4	-105.2	-1.8	-105.6	-2.2
CH ₃ COF (acetyl fluoride)	-105.7	-109.0	-3.3	-109.3	-3.6
CH ₃ COCl (acetyl chloride)	-58.0	-62.7	-4.7	-63.1	-5.1
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-35.5	-4.0	-35.8	-4.3

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Table B.3 – continued from previous page

Molecule	Expt.	PBE0-EXX		PBE0-HFX	
	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ$	Deviation	$\Delta_f H_{298}^\circ$	Deviation
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-65.4	-0.2	-65.8	-0.6
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-53.3	-1.6	-53.7	-2.0
(CH ₃) ₃ N (trimethylamine)	-5.7	-8.7	-3.0	-9.1	-3.4
C ₄ H ₄ O (furan)	-8.3	-21.0	-12.7	-21.4	-13.1
C ₄ H ₄ S (thiophene)	27.5	14.8	-12.7	14.4	-13.1
C ₄ H ₅ N (pyrrole)	25.9	10.1	-15.8	9.8	-16.1
C ₅ H ₅ N (pyridine)	33.6	14.5	-19.1	14.1	-19.5
H ₂	0.0	5.2	5.2	5.2	5.2
SH	34.2	34.6	0.4	34.6	0.4
C≡CH (² A', C _s)	135.1	134.0	-1.1	134.0	-1.1
CH=CH ₂ (² A', C _s)	71.6	66.5	-5.1	66.3	-5.3
CH ₃ CO (² A', C _s)	-2.4	-7.6	-5.2	-7.8	-5.4
CH ₂ OH (² A, C ₁)	-4.1	-5.5	-1.4	-5.6	-1.5
CH ₃ O (² A', C _s)	4.1	1.4	-2.7	1.1	-3.0
CH ₃ CH ₂ O (² A'', C _s)	-3.7	-9.5	-5.8	-9.9	-6.2
CH ₃ S (² A', C _s)	29.8	26.6	-3.2	26.4	-3.4
CH ₃ CH ₂ (² A', C _s)	28.9	24.7	-4.2	24.5	-4.4
(CH ₃) ₂ CH (² A', C _s)	21.5	14.5	-7.0	14.2	-7.3
(CH ₃) ₃ C (<i>t</i> -butyl radical, C _{3v})	12.3	4.2	-8.1	3.8	-8.5
NO ₂	7.9	1.3	-6.6	0.9	-7.0

Curriculum Vitae

Name:	Liyuan Ye	
Post-Secondary Education and Degrees:	University of Toronto Scarborough 2011 – 2016 B.Sc. Thesis title: “Geometric phase effects in the non-adiabatic dynamics through $^1A_2 - S_0$ and $^1B_1 - S_0$ conical intersections of pyrrole”	Scarborough, ON
	University of Western Ontario 2018 – 2020 M.Sc. Thesis title: “Hybrid density functionals with proper exact exchange”	London, ON
Related Work Experience:	Teaching Assistant: Linear Algebra University of Toronto Scarborough ◊ Held weekly tutorials and office hours ◊ Marked weekly quizzes and midterm/final exams	2014 – 2015
	Teaching Assistant: Introduction to Physics University of Toronto Scarborough ◊ Held weekly practical session to guide students in group solving problem sets and conducting 2 experiments during the term ◊ Marked and made comments on problem sets done in practical sessions and lab reports; Marked midterm exam	2014
	Teaching Assistant: First Year Chemistry Lab The University of Western Ontario ◊ Supervised students to conduct experiments safely and finish on time ◊ Marked the student’s lab reports and provided them feedbacks	2018 – 2020
Graduate Courses Taken:	Computational Quantum Chemistry Statistical Mechanics	

Publication:

R. Gherib, L. Ye, I. G. Ryabinkin and A. F. Izmaylov, “On the inclusion of the diagonal Born-Oppenheimer correction in surface hopping methods,” *J. Chem. Phys.* **144**, 154103 (2016).

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